Photoluminescent Properties of Cadmium Selenide in Contact with Solutions and Films of Vaska's Complex: Effects of Oxygen and Carbon Monoxide[†]

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The band-edge photoluminescence (PL) intensity of etched n-CdSe single crystals is reversibly enhanced in the presence of nitrogen-saturated toluene solutions of *trans*-IrCl(CO)(PPh$_3$)$_2$, Vaska's complex (**1**), relative to nitrogen-saturated toluene alone. The PL enhancement is indicative of adsorption of a Lewis base onto the n-CdSe crystals. When the toluene solution of **1** is saturated with carbon monoxide, repetition of these experiments produces larger reversible PL enhancements; when the same solution is saturated with oxygen, large reversible quenching is observed relative to toluene. These PL intensity changes are attributed to binding to the surface of **1·CO** and **1·O$_2$**, the CO and O$_2$ adducts of **1**, respectively. The concentration-dependent PL changes are well fit by the Langmuir adsorption isotherm model; responses to **1** and **1·CO** are characterized by similar binding constants K of nearly 10^5 M^{-1}, while K for **1·O$_2$** is 10^7 M^{-1}. In the solid state, **1** is known to bind CO and O$_2$ reversibly. When the CdSe surface is coated with thin films of **1**, evaporated from toluene solution, CO and O$_2$ gases can be detected through reversible enhancement and quenching, respectively, of CdSe PL intensity relative to a gaseous nitrogen ambient; neither gas affects the PL intensity of uncoated CdSe samples appreciably. Films of **1** coated onto NaCl plates or CdSe crystals yield binding constants for CO from IR spectral changes that are experimentally indistinguishable from those obtained by PL measurements, ∼10^2 M^{-1}. In contrast, the binding constant for O$_2$, determined from IR spectral changes to be ∼10^2 M^{-1}, is roughly an order of magnitude lower than that estimated from PL changes, evidencing a roughly 10-fold enhancement in binding affinity at the semiconductor−film interface for **1** toward O$_2$ relative to the bulk film environment. Aspects of the coordination chemistry of **1** that may account for these electrooptical effects are discussed.

Introduction

We have demonstrated that the band-edge photoluminescence (PL) intensity of single-crystal n-CdSe samples can be reversibly perturbed by adsorption and desorption of a broad variety of gaseous and solution phase species.[1] Typically, Lewis acids have been found to quench PL intensity and Lewis bases to enhance it relative to a reference ambient, defining a type of "luminescent litmus test" for adsorbates. These effects may permit on-line sensing of, for example, precursor gases used in the growth of materials by chemical vapor deposition.[1a]

For analytes that do not elicit a PL response from the etched n-CdSe sample relative to a reference ambient, we have recently shown that a film coated onto the solid can serve as a transducer that produces an analyte-driven PL response. Thus, when CdSe is coated with a Co(II) macrocycle known to bind dioxygen reversibly in the solid state, the PL is found to be quenched reversibly relative to a nitrogen ambient.[2]
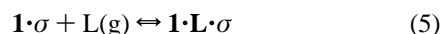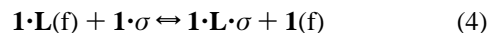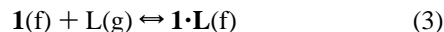
In this paper we report the extension of this methodology using films of Vaska's complex, *trans*-IrCl(CO)(PPh$_3$)$_2$, **1**. This coordinatively unsaturated, 16-electron Ir(I) complex is known to possess a rich complexation chemistry based on ligand addition and oxidative addition reactions.[3] For example, in solution, the complex reversibly binds dioxygen and carbon monoxide, eq 1, leading to the structures illustrated in Chart 1.[4−6] In the solid state, the decomposition of the dioxygen

$$1 + L \rightleftharpoons 1 \cdot L; \qquad L = O_2, CO \qquad (1)$$

adduct of **1**, **1·O$_2$**, has been studied, and reversible binding of dioxygen and carbon monoxide by polyethylene matrices containing **1** has been reported.[7,8]

We report in this paper that nitrogen-saturated toluene solutions of **1** enhance the PL intensity of n-CdSe relative to nitrogen-saturated toluene alone. The perturbation is also ligand dependent: relative to nitrogen-saturated toluene solutions of **1**, CO-saturated solutions of **1** cause reversible PL enhancement and O$_2$-saturated solutions of **1** cause reversible PL quenching. These adsorption reactions from solution can be represented by eq 2, where σ is a surface site.

$$\sigma + A \rightleftharpoons A \cdot \sigma; \qquad A = 1, 1 \cdot CO, \text{ and } 1 \cdot O_2 \qquad (2)$$
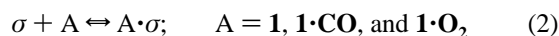
Likewise, films of **1** on CdSe, prepared from toluene solution by solvent evaporation, permit reversible enhancement and quenching of PL intensity from exposure to CO and O$_2$, respectively, relative to a nitrogen ambient; no PL response to these gases is seen for uncoated CdSe samples. The film-mediated reaction can be thought of as involving dissolution of the gas in the film, eq 3, followed by adsorption onto the semiconductor, eq 4, leading to the overall reaction, eq 5.

$$1(f) + L(g) \rightleftharpoons 1 \cdot L(f) \qquad (3)$$

$$1 \cdot L(f) + 1 \cdot \sigma \rightleftharpoons 1 \cdot L \cdot \sigma + 1(f) \qquad (4)$$

$$1 \cdot \sigma + L(g) \rightleftharpoons 1 \cdot L \cdot \sigma \qquad (5)$$

In toluene solution, equilibrium binding constants K for adsorption onto CdSe, eq 2, are similar for **1** and for **1·CO**, but about 2 orders of magnitude larger for **1·O$_2$**. Similarly, films of **1** on CdSe substrates yield semiconductor−film interfaces that bind O$_2$ more strongly than CO by an order of magnitude,
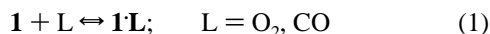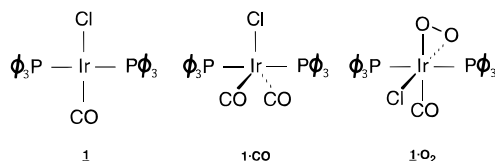

CHART 1

based on values of K for eq 5 estimated from PL measurements; by infrared measurements, which can be used to estimate values of K for the equilibrium of eq 3, both O_2 and CO exhibit similar binding constants. The derived distribution coefficients, represented by eq 4, indicate that CO shows little preference in partitioning itself between the bulk film and the semiconductor surface, whereas O_2 has a clear preference for the film−semiconductor interface. We also demonstrate that films of **1·O₂** are photoactive: release of dioxygen is facilitated by short wavelength visible excitation. The electrooptical properties of these interfaces can be interpreted in terms of the coordination chemistry of **1**.

Experimental Section

Materials and Sample Preparation. Samples of Vaska's complex, *trans*-IrCl(CO)(PPh₃)₂, **1**, were purchased from Aldrich and used without further purification. Carbon monoxide (99.0%) and oxygen (99.6%) gases were obtained from Liquid Carbonic Specialty Gas Corporation. Both gases were used as received. Toluene (EM Science, 99+%) was refluxed over CaH_2 and collected under dry N_2. Films used for IR studies (vide infra) were prepared from anhydrous chloroform (EM Science, 99+%) through which dry N_2 was bubbled prior to dissolving **1** in this solvent. Single crystals of vapor grown, *c*-oriented n-CdSe with resistivities of $\sim$2 Ω cm were obtained from Cleveland Crystals, Inc., Cleveland, OH. CdSe crystals were etched in a Br_2/MeOH etch (1:15 v/v) until the shiny, Cd-rich side of the crystal was revealed; crystals then were stored in a dry, N_2-filled glovebag when not in use. Films of **1** for PL experiments were prepared in a dry nitrogen atmosphere by making $\sim$200 μM toluene solutions of **1**, dipping a freshly etched CdSe crystal into the solution, rinsing with toluene solvent, and then drying the surface in flowing nitrogen. Alternatively, the films were prepared by spreading a small drop of the solution of **1** over the surface of an etched n-CdSe crystal and allowing the solvent to evaporate. Both techniques gave similar results and produced films of $\sim$200 Å in thickness, assuming uniform coverage.

Apparatus. A gas flow apparatus was constructed from Tygon tubing that allowed a mixture of N_2 and the gaseous analyte to flow over the semiconductor surface while the solid was illuminated.[1] Partial pressures of the gases were controlled by adjusting the flow rates of the incoming gases. Total gas flow rates varied from 100 to 180 mL/min, and total gas pressure was 1 atm.

The CdSe sample was mounted on a glass rod between two Teflon spacers within a glass tube.[9] The sample cell was designed to accommodate flowing gas mixtures as well as introduction and drainage of solutions. The cell was mounted in a stable configuration that allowed introduction of gases and solutions without disturbing the optical alignment.

Optical Measurements. A Coherent Innova 90-5 Ar^+ laser (457.9 and 514.5 nm) or a Spectra-Physics He−Ne laser (632.8 nm) provided excitation of the semiconductor. Incident intensities ranged from 1 to 20 mW/cm². Emission spectra were monitored using an Oriel Instaspec II silicon diode array spectrophotometer. The setup allowed simultaneous monitoring

of the full PL spectrum and the PL intensity at a particular wavelength versus time. To further exclude background light from the detector while allowing band-edge PL ($E_g \approx 1.7$ eV; $\lambda_{max} \approx 720$ nm) to pass, a red cutoff filter was inserted into the spectrophotometer. The signal collected was then available for computer analysis. Solid-state absorption spectra of **1** and its adducts were obtained by evaporating a thin film onto a glass slide from toluene solution and inserting the slide into a Cary 17D spectrophotometer; assuming uniform thickness, the film-forming procedures employed lead to a film of $\sim$5 μm thickness. Solution spectra were obtained both on this instrument and on a Hewlett-Packard HP89530A spectrophotometer.

Infrared Measurements. Films used in IR absorption experiments were prepared in a manner similar to those used for PL and electronic spectral measurements: drops of $\sim$400 μM solutions of **1** in toluene or chloroform were placed on the surface of a NaCl window or n-CdSe crystal and dried in an N_2 atmosphere; the n-CdSe crystals were slightly roughened with 320 grit sandpaper to promote film adhesion. The gas-metering apparatus described above was attached to a desiccated chamber containing the film samples, which was then purged for 30 min to establish the desired gaseous ambient. The chamber was then sealed, and the films were permitted to come to equilibrium with the ambient atmosphere. Films were removed from the chamber and immediately placed in a Nicolet 740 FTIR spectrometer to measure the infrared absorption spectrum before significant loss of gas from the film could occur. For oxygenated films, loss of O_2 is sufficiently slow that it is negligible. For films of **1·CO**, the loss of CO was more rapid, and the values of equilibrium binding constants reported here more accurately represent lower limits, with true values estimated to be not more than $\sim$30% higher. Data were processed using Nicolet Advantage software.

A quantitative analysis of ligand uptake in films of **1** was made using IR absorption data. The reaction of the film with CO and O_2 was monitored by exposing the film to the gases and observing the change in the IR spectrum. Beginning with a film of **1** and introducing mixtures of CO or O_2 with N_2 gas into the atmosphere above the film, a decrease in the CO absorption peak of **1** at 1956 cm⁻¹ is seen, with a corresponding growth of a peak at 2000 cm⁻¹ for **1·O₂** or of peaks at 1924 and 1972 cm⁻¹ for **1·CO**. Integrated absorption intensities were used in calculations.
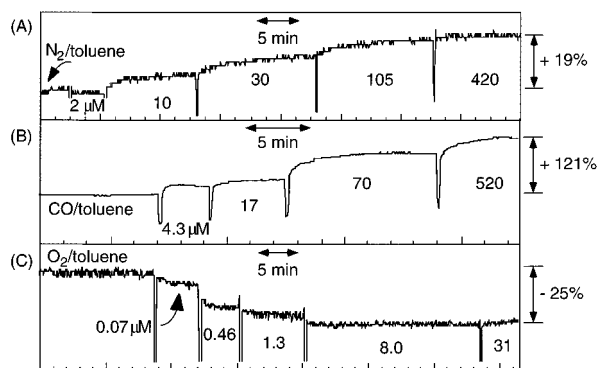
Monitoring the characteristic IR peaks permitted an estimate of the adduct formation equilibrium constant K for eq 3. Calvin and co-workers studied a similar system wherein gaseous oxygen reversibly reacted with a cobalt macrocycle complex and found that the oxygen adduct was essentially dissolved in the matrix of the macrocycle.[10] A similar treatment of this system as a solid solution of **1** and **1·L** permits an estimate of binding constants K for eq 3, using eq 6:

$$K = \left[\frac{A_a}{A_v}\right]\left[\frac{\epsilon_v}{\epsilon_a}\right]\frac{1}{P_g} \qquad (6)$$

Here, A_a and A_v are the integrated absorption intensities of the adduct (**1·L**) and adduct-free (**1**) complexes' CO stretching peaks, respectively; $[\epsilon_v/\epsilon_a]$ is the ratio of extinction coefficients for these species, and P_g is the partial pressure of CO or O_2 above the film.

The ratio of extinction coefficients $[\epsilon_v/\epsilon_a]$ was calculated from the dependence of the integrated peak absorption intensities on species concentration, using the relationship of eq 7:

$$[\epsilon_v/\epsilon_a] = [A_v/C_v l_v]/[A_a/C_a l_a] \qquad (7)$$

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Figure 1. Changes in PL intensity of an etched n-CdSe crystal resulting from exposure to increasing concentrations of Vaska's complex dissolved in (A) nitrogen-, (B) carbon monoxide-, and (C) oxygen-saturated toluene. The downward spikes are transients caused by draining the sample cell when changing solutions. The PL was excited with 514-nm light and monitored at 720 nm. Panels A, B, and C are data from three different CdSe samples.

Here, C_v and C_a are the concentrations of **1** and **1·L**, respectively, and l_a and l_v are the corresponding film thicknesses. Assuming that $l_a = l_v$ (the film thickness is unaffected by gas uptake; from ref 6, densities of **1** and its CO and O$_2$ adducts differ by less than 10%) and that all **1** is converted to **1·L** ($\Delta C_v = -\Delta C_a$), then eq 7 reduces to eq 8:

$$[\epsilon_v/\epsilon_a] = -\Delta A_v/\Delta A_a \qquad (8)$$

where ΔA_v and ΔA_a are the changes in integrated absorption intensities for **1** and **1·L**, respectively. Values for this ratio of 1.5 ± 0.3 and 0.63 ± 0.12 were measured for several pressures of O$_2$ and CO, respectively. These ratios can be substituted into eq 6 to obtain values of K. Because of the overlap of one band of **1·CO** with the band of **1**, its contribution to the spectrum of **1** was estimated from the integrated intensity of the nonoverlapping band and subtracted prior to estimating the value of K using eq 6.

To characterize the species present in solution PL studies, O$_2$- and CO-saturated toluene solutions containing the maximum concentration of **1** used in PL experiments were examined. The O$_2$ adduct exhibited a band at 2009 cm^{-1}, and the CO adduct displayed bands at 1930 and 1983 cm^{-1}, values similar to those reported in the literature.[4,5] Only these peaks were observed in 2 mM toluene solutions of **1** that were saturated with these gases.

Results and Discussion

Samples of CdSe emit red band-edge PL ($E_g \approx 1.7$ eV; $\lambda_{max} \approx 720$ nm) when excited by ultra-band-gap light at room temperature. The samples show negligible PL intensity changes referenced to N$_2$ when exposed to CO or O$_2$, either in the gas phase or while immersed in toluene solution. However, in the presence of a film or toluene solution of **1**, addition of CO to the sample cell causes a reversible enhancement of CdSe PL intensity, while the presence of O$_2$ quenches the PL intensity reversibly. The following sections detail the reactions of CO and O$_2$ with solutions and films of **1**, using PL changes to estimate adduct-induced changes in depletion width and PL and IR changes to estimate equilibrium binding constants. The final section examines aspects of the coordination chemistry of **1** that may produce the observed electrooptical effects.

I. Solution Studies. *Surface Interactions.* When the shiny, Cd-rich, (0001) surface of a CdSe single crystal is exposed to nitrogen-saturated toluene solutions of **1**, the crystal's PL intensity is reversibly enhanced. As shown in Figure 1, part

A, the effect is easily discernible at a concentration of 10 μM and saturates at $\sim$500 μM. Because the PL spectral distribution is unaffected under our experimental conditions, these changes can be monitored at a single wavelength, the PL band maximum.

As we have noted in prior studies, such an enhancement of PL intensity is consistent with the adsorption of a Lewis base onto the CdSe surface and the formation of a weak charge-transfer complex.[1a] Coordinatively unsaturated surface atoms could provide intra-band-gap surface states that are filled to the Fermi level with electrons from the semiconductor bulk. Electron density donated from **1** could cause electrons trapped at the surface to move back into the bulk, decreasing the width of the surface depletion region. Treating this region as nonemissive, because electron−hole pairs created by the exciting light will be swept apart by the electric field present and prevented from recombining, implies that adsorption of a Lewis base will enhance the PL intensity by reducing the depletion width.

Repetition of this experiment using CO-saturated toluene permits an evaluation of the impact of the adduct reaction, eq 1, on the adsorption equilibrium, eq 2. In the absence of **1** in toluene, dissolved CO has no influence on PL intensity at a concentration of $\sim$8 mM.[11] Consistent with the large reported binding constant of **1** for CO ($\sim$10^3 M^{-1} in chlorobenzene), the IR spectrum of the CO-saturated solution reveals only the presence of **1·CO**.[3a] We find that the PL changes in the presence of CO mimic those in N$_2$-saturated solution (Figure 1, part B), except that the saturated enhancement is invariably larger. Whether this reflects greater basicity and/or a different kind of surface coverage cannot be determined by our methodology. The kinetics of adsorption and desorption are also somewhat faster for **1·CO** than for **1** in toluene.

In contrast to the effects seen in N$_2$- and CO-saturated toluene solutions of **1**, use of O$_2$-saturated solutions led to a quenching of the PL intensity, Figure 1, part C; in the absence of **1** in toluene, dissolved O$_2$ has no influence on PL intensity at a concentration of $\sim$9 mM.[11] As with CO, IR data revealed only **1·O$_2$** in solution, consistent with the large reported value of K for eq 1, $\sim$10^4 M^{-1} in chlorobenzene.[3a] On the basis of previous studies, we interpret the PL quenching as consistent with adsorption of a Lewis acidic species, which can draw additional electron density from the bulk to surface states, thereby expanding the depletion region and reducing the PL intensity.[1b] That **1·O$_2$** acts as a Lewis acid is consistent with its formal oxidation relative to **1**. Adsorption of **1·O$_2$** onto the surface is slower than that of **1·CO**, but faster than that of **1**, based on PL changes. The rate of desorption for **1·O$_2$** was roughly comparable to that of **1**.

Dead-Layer Model. Quantitative estimates of the change in the depletion width caused by adsorption of **1**, **1·CO**, and **1·O$_2$** onto the CdSe surface can be made using a dead-layer model, which assumes that a zone of the order of the depletion region is nonemissive because of the absence of electron−hole pair recombination therein.[12,13] This assumption leads to eq 9:

$$PL_{ref}/PL_x = \exp(-\alpha'\Delta D) \qquad (9)$$

Here, PL_{ref} is the PL intensity in a reference ambient (N$_2$-saturated toluene) and PL_x is the PL intensity in the presence of the adsorbate; $\alpha' = (\alpha + \beta)$ where α and β are the absorptivities for excitation and emission wavelengths for CdSe, respectively (β is taken to be 1.2×10^4 cm^{-1} at 720 nm[14]); and ΔD is the change in dead-layer thickness. The dead-layer model assumes that there is either no change in surface recombination velocity S accompanying adsorption or that it remains large before and after adsorption ($S \gg L/\tau$ and $S \gg \alpha L^2/\tau$, where L

TABLE 1: Summary of Dead-Layer Model Results[a]

complex	λ_{ex},[b] nm	$1/\alpha$,[c] Å	PL ratio[d]	ΔD,[e] Å
solutions				
1	458	570	1.27	−130
	514	740	1.26	−160
	633	1500	1.15	−180
1·CO	458	570	2.17	−410
	514	740	1.88	−430
	633	1500	1.38	−410
1·O$_2$	458	570	0.84	90
	514	740	0.85	110
	633	1500	0.92	110
film				
1·CO	458	570	1.50	−210
	514	740	1.33	−190
	633	1500	1.17	−200
1·O$_2$	458	570	0.57	300
	514	740	0.64	300
	633	1500	0.73	400

[a] Analysis of maximum adsorbate-induced changes in band-edge PL intensity of an etched n-CdSe crystal. The solution measurements correspond to use of nitrogen-saturated (**1**), carbon monoxide-saturated (**1·CO**), and oxygen-saturated (**1·O$_2$**) toluene solutions and were performed on the same sample. Film measurements were performed on the same film sample. [b] Excitation wavelength. [c] Values of the optical penetration depth of the incident light, given as the reciprocal of the absorptivity.[14] [d] Ratio of CdSe PL intensity in toluene solutions of the indicated complex relative to PL intensity in gas-saturated toluene alone (solution data) and, for film data, PL intensity in ∼50% mixtures of the analyte with N$_2$ relative to pure N$_2$ gas (total pressure of 1 atm). [e] Contractions (negative values) or expansions (positive values) in dead-layer thickness upon passing from reference to analyte environments, calculated from eq 9. Values are ±10%.

and τ are the minority carrier diffusion length and lifetime, respectively). The model predicts that the ΔD value obtained for adsorption of a particular species is independent of excitation wavelength. Adherence to the model was tested by varying excitation wavelengths between 458 and 633 nm. Table 1 demonstrates that reasonable fits to the model were obtained for toluene solutions of **1**, **1·CO**, and **1·O$_2$**. The first two species contract the dead-layer thickness by ∼150 and 400 Å, respectively, and the dioxygen adduct expands it by ∼100 Å.

Adsorption Binding Constants. The Langmuir adsorption isotherm model can be used to estimate adsorbate binding constants for **1**, **1·CO**, and **1·O$_2$** onto CdSe, eq 2, through the concentration dependence of the PL changes. Using θ to represent the fractional surface coverage, the quantitative form of the Langmuir model is given by eq 10:[15]

$$\theta = (KC/(1+KC)) \text{ or } 1/\theta = (1/KC) + 1 \qquad (10)$$

Here, K is the equilibrium constant for adsorption and C is the molar concentration. The PL changes are used to estimate θ: maximum surface coverage, $\theta = 1$, is assumed when the PL intensity changes have saturated, PL$_{sat}$, while $\theta = 0$ corresponds to the PL intensity in the reference ambient, PL$_{ref}$. Intermediate values for θ are estimated as the fractional change in dead-layer thickness, eq 11:

$$\theta = \ln[\text{PL}_{ref}/\text{PL}_x]/\ln[\text{PL}_{ref}/\text{PL}_{sat}] \qquad (11)$$

A double-reciprocal plot of θ^{-1} versus C^{-1} is shown in Figure 2 for **1**; the extracted values of K for eq 2 for **1**, **1·CO**, and **1·O$_2$** are collected in Table 2. Note that **1** and **1·CO** give roughly comparable values of nearly 10^5 M^{-1} but that **1·O$_2$** binds much more strongly with K approaching 10^7 M^{-1}. The presence of **1·O$_2$** can be detected at concentrations of less than 0.1 μM.
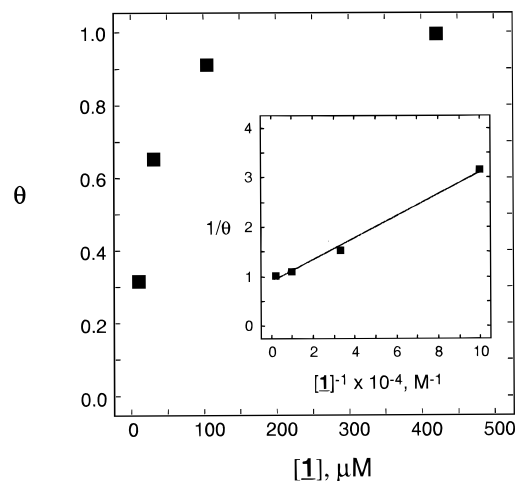
Figure 2. Plot of the fractional surface coverage θ versus concentration of **1** in N$_2$-saturated toluene at 25 °C; values of θ are estimated from eq 11. The linearity of the double-reciprocal plot shown in the inset implies good agreement with the Langmuir adsorption isotherm model, eq 10. The binding constant K, extracted from the double-reciprocal plot, is $(5 \pm 1) \times 10^4$ M^{-1}. The excitation wavelength employed was 514 nm.
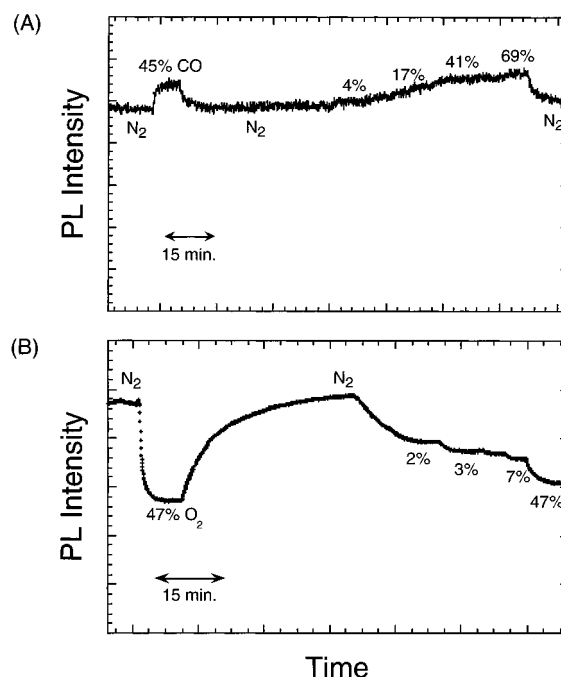
Figure 3. PL intensity changes of an etched n-CdSe crystal coated with a film of **1** when exposed to (A) carbon monoxide and (B) oxygen gases. PL intensity is essentially unchanged relative to the nitrogen ambient when an uncoated crystal is exposed to these two gases. PL was excited with 514-nm light and monitored at 720 nm.

II. Film Studies. *Surface Interactions.* Exposure of the bare CdSe surface to CO and O$_2$ gases causes a negligible PL modulation relative to the PL intensity in the presence of N$_2$. However, films of **1** evaporated from toluene solution onto CdSe surfaces can serve as analyte-driven transducers for effecting PL responses from the substrate in accord with the chemistry of eqs 3−5. Films employed in our studies have thicknesses of ∼200 Å if uniform deposition is assumed. Paralleling the solution results, when film-coated CdSe samples were exposed to CO and O$_2$ gases, they exhibited reversible PL enhancement and quenching, respectively, relative to the intensity in the nitrogen reference ambient, as shown in Figure 3.

Dead-Layer Model. Table 1 shows that the film-coated samples yielded a good fit to the dead-layer model for CO

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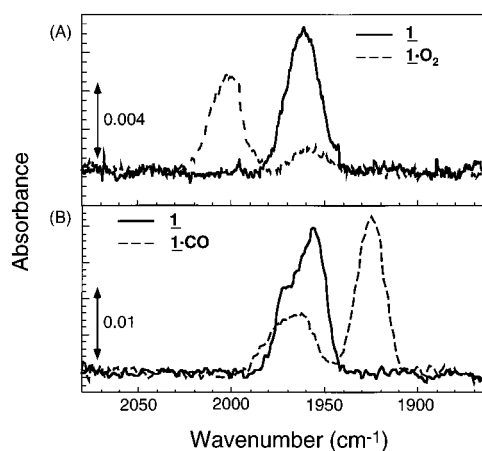
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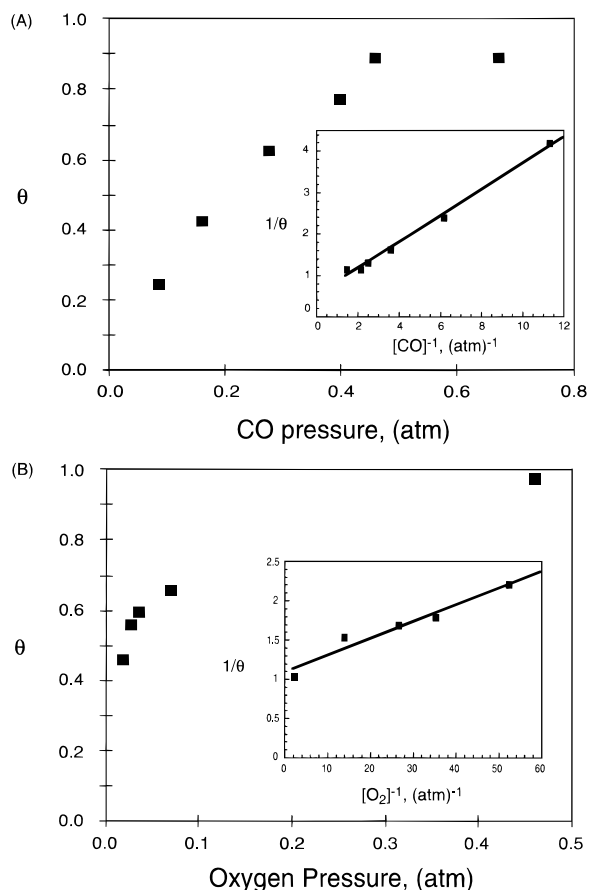
Figure 4. Plot of θ, based on PL changes (eq 11), versus concentration of (A) carbon monoxide and (B) oxygen gases for a sample of CdSe coated with **1**. Equilibrium constants calculated at 25 °C for carbon monoxide and oxygen, eqs 5 and 10, are 76 ± 16 M^{-1} (3.1 ± 0.7 atm^{-1}) and 1100 ± 200 M^{-1} (45 ± 8 atm^{-1}), respectively. The excitation wavelength was 514 nm.

Figure 5. Infrared absorption spectra in the carbonyl stretching region of a film of **1** on a NaCl window in different gaseous ambients: 1 atm in N_2 (solid line), O_2 (dashed line, panel A), and CO (dashed line, panel B). Note that there is still some uncomplexed **1** at 1 atm in the O_2 experiment.

TABLE 2: Equilibrium Binding Constants

complex	K^c (M^{-1}) PL	K^d (M^{-1}) IR
solution[a]		
1	(5 ± 1) × 10^4	
1·CO	(8 ± 2) × 10^4	
1·O$_2$	(400 ± 100) × 10^4	
film[b]		
1·CO	76 ± 16	30 ± 9[e]
1·O$_2$	1100 ± 200	78 ± 24

[a] Complexes dissolved in toluene saturated with nitrogen (**1**), carbon monoxide (**1·CO**), and oxygen (**1·O$_2$**). The data were determined using the same CdSe sample. [b] Films of **1** on CdSe crystals (PL experiments) or NaCl windows (IR experiments); use of CdSe plates as IR windows yielded similar results. Data for the PL experiments were determined using the same film sample. [c] Equilibrium constants for eq 2 (solution data) and eq 5 (film data), determined from fits to the Langmuir adsorption isotherm model, using changes in PL intensity, eqs 10 and 11. Values of K were in the range of (4–7) × 10^4 M^{-1} for solutions of **1**, and (4–6) × 10^6 M^{-1} for solutions of **1·O$_2$** using several samples. [d] Equilibrium constants for uptake of gases by a film of **1**, determined from IR absorption measurements, eqs 3 and 6. Values were in the range of 22–37 M^{-1} for **1·CO** and 70–120 M^{-1} for **1·O$_2$** using several samples. [e] Represents a lower limit for K. See Experimental Section.

adsorption and a poorer fit for O_2, which may reflect film photochemistry (vide infra). Relative to an ambient of nitrogen gas, CO uptake by the film caused a maximum reduction in ΔD of ~200 Å. The oxygen-induced expansion in ΔD appears to be at least 300 Å.

Binding Characteristics. Figure 4 displays Langmuir adsorption isotherm plots for uptake of gaseous CO and O_2 onto **1**-coated CdSe samples. Good fits were found from PL changes, and the binding constants extracted (vide infra) are included in Table 2. Over a range of samples, we find equilibrium constants from 50 to 170 M^{-1} (~2–7 atm^{-1}) for CO and from 1000 to 1200 M^{-1} (~40–50 atm^{-1}) for O_2.

A measurement of the equilibrium constant for uptake of O_2 and CO by the film, eq 3, can be made by coating **1** onto a NaCl infrared window or CdSe crystal and observing the spectral changes in the carbonyl stretching region when the film is exposed to CO and O_2. Figure 5 displays these changes, which can be used to estimate the fraction of the film present as **1·CO** or **1·O$_2$** at various partial pressures of CO or O_2. Values of K for eq 3 are collected in Table 2. Although the data shown are for NaCl substrates, use of a CdSe window yielded similar values of K.

For the CO adduct, the PL and IR spectral changes monitored exhibit a similar concentration profile, Figure 6, leading to a similar value for K for eqs 3 and 5; this leads to an estimated value of K for the distribution coefficient for eq 4 of roughly unity, i.e., no strong preference for CO to be in the film vs at the semiconductor–film interface. However, in sharp contrast, the PL and IR spectral changes monitored for the O_2 adduct

have strikingly different concentration profiles: the onset and saturation of response are seen by PL at order of magnitude lower concentrations than those by IR, corresponding to an order of magnitude larger value of K for eq 5 compared to eq 3. The value estimated for K for eq 4 is thus about 10 and suggests an enhanced binding affinity for O_2 at the semiconductor–film interface relative to the film.

The film reactions of eqs 3–5 are reversible on a time scale ranging from a few minutes for carbon monoxide to several hours for oxygen. Reversible responses to CO have been observed for months for films stored under dry N_2 with little degradation. Smaller, reversible PL modulations were still observable for up to 2 weeks after films had been repeatedly exposed to O_2. However, when a film had been exposed to O_2 gas while under sustained 514-nm illumination, the PL response to CO gas was significantly degraded, which we attribute to photochemical decomposition of the O_2 adduct films (vide infra).[4,16]

The kinetic and thermodynamic features of the film's response to CO and O_2 could be directly observed in a competition experiment since these two gases produce opposite PL signatures. We found that when equal partial pressures of CO and

(A)

(B)
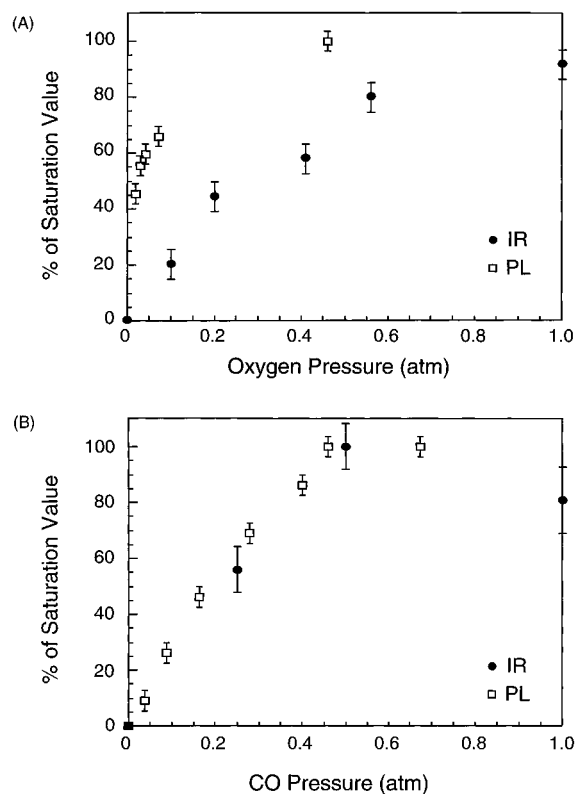
Figure 6. Normalized infrared responses of a film of **1** on a NaCl plate and of PL responses of a film of **1** on CdSe to changes in (A) oxygen and (B) carbon monoxide partial pressure. Responses were normalized so that values of the integrated absorption peak intensity (for the IR experiments) and dead-layer thickness (for the PL experiments) at saturation were set to be 100%; intermediate values are expressed as percentages of the saturation value. See Table 2 for values of K extracted from these experiments.
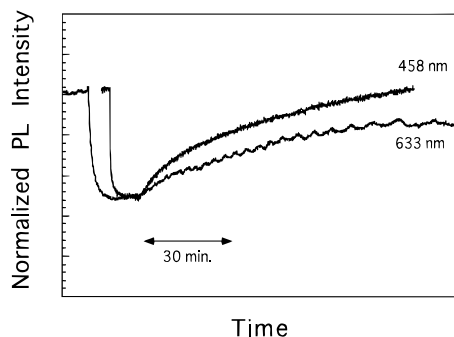

Figure 7. Dependence of PL response on excitation wavelength. The desorption of O_2 from CdSe crystals coated with films of **1** is much faster when using 458-nm light than 633-nm light. The PL responses have been normalized to the same fractional change with both wavelengths. The oxygen response requires several hours to fully reverse under 633-nm illumination. The laser intensity was 10 mW/cm^2 in both experiments.

O_2 flowed over the coated surface, a PL enhancement was initially observed, due to the quicker response of the film to CO. Subsequently, a substantial net quenching of PL intensity was observed as the more thermodynamically stable O_2 adduct (based on PL-derived values of K for eq 5) dominated the response. Returning to a nitrogen ambient restored the original PL base line intensity.

Film Photoreactivity. We have found that the rate of release of O_2 from films of **1·O₂** is a wavelength dependent process. Figure 7 shows the PL intensity as a function of time, with 458- and 633-nm excitation, when an oxygenated film is returned to a nitrogen ambient. With 458-nm light, the return

SCHEME 1: Possible Binding Mode of 1·O₂ at the CdSe Surface
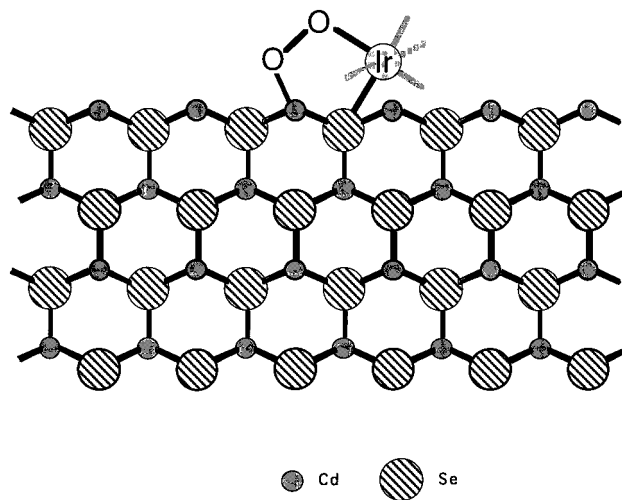
to the PL intensity base line is much faster than when the sample is interrogated with 633-nm light. An orange film of the O_2 adduct deposited on a glass slide (see Experimental Section) has a small amount of absorption at 458 nm but is transparent at 633 nm. Photoassisted dissociation of O_2 from the film could account for the poor fit to the dead-layer model observed for films exposed to O_2: as shown in Table 1, the value of ΔD decreases with shorter excitation wavelength. This is the trend that would be expected if absorption of light by the film causes release of dioxygen.[2] Also consistent with this hypothesis is the lack of a similar wavelength effect for the CO adduct, which yielded a much better fit to the dead-layer model. The absorption spectrum for the CO adduct of the film shows that the film is essentially transparent throughout the visible spectrum.

III. Aspects of Complexation. There are three features of note that hinge on the complexation chemistry of **1**: (1) the direction and magnitude of the PL responses; (2) the differences between solution and film environments; (3) the differences in distribution coefficients (eq 4) for the CO and O_2 adducts.

Vaska's complex is well-known for its ability to coordinate a wide variety of ligands to the iridium atom.[3] In solution, the electron density and coordination sites available at the formally Ir(I) center[3a] could enable the complex to act like a Lewis base toward Lewis acidic sites on the CdSe surface, presumably Cd atoms, leading to the observed increase in PL intensity in nitrogen-saturated toluene solution. Shriver et al. have reported the reaction of **1** with a variety of Lewis acids in benzene solution and have isolated solid adduct complexes.[17] In CO-saturated solution, the five-coordinate species **1·CO** is present. The further increase in PL intensity observed with **1·CO** suggests that it can deliver additional electron density relative to **1** and/or that there is a different kind of surface coverage.

When oxygen-saturated solutions were used, **1·O₂** is present in solution, and a Lewis acidic PL response is seen. The Ir center can be regarded as being oxidized in **1·O₂**, based on the IR carbonyl stretching frequency shift to higher energy.[3a] With respect to the structure of the **1·O₂**/surface interaction, there are few examples of seven-coordinate iridium species in the literature, and those generally involve smaller ligands.[18] One possible model for **1·O₂** binding involves chelation, as shown in Scheme 1. Previous studies have provided evidence for surface chelation through the observation of enhanced binding constants, such as are seen here.[19] The stability of a five-membered chelating ring formed with the CdSe surface could

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account for the increased affinity of the surface for $1 \cdot O_2$ relative to that for **1** and $1 \cdot CO$. A scheme in which the iridium accepts electron density from a surface selenium atom and one of the oxygen atoms donates electron density to a Cd atom could be consistent with the net acidic interaction observed.[20]

The PL effects observed in solution are to some extent paralleled in the film studies: CO and O_2 ambients give enhancement and quenching relative to an N_2 reference ambient, Table 1. We might expect that PL changes in the film system derive from the $1 \cdot CO$ and $1 \cdot O_2$ species positioned most closely to the CdSe surface. The similar direction for PL changes in film and solution environments suggests that some of the same kind of interactions are present at both solution−semiconductor and film−semiconductor interfaces.

Finally, the distribution coefficients, eq 4, for $1 \cdot O_2$ and $1 \cdot CO$ are noteworthy. In comparing the CO and O_2 adducts of **1**, the CO adduct is only five-coordinate, whereas the O_2 adduct is six-coordinate. The CO adduct may have the steric freedom at the semiconductor surface to adopt a geometry at this film−semiconductor interface that is similar to its structure in the bulk solid, leading to a similar binding constant by both IR and PL methods and the near-unity value for K for eq 4. On the other hand, the O_2 adduct may form a chelating ring with the surface as in Scheme 1, as proposed for the binding mode from solution, leading to the estimated order of magnitude larger value for K in eq 4. Although our present methods cannot reveal the interfacial structural details for $1 \cdot O_2$, ring formation could enhance binding near the interface, as reflected in the much larger value of K determined by PL measurements.

Note Added in Proof: We have recently shown that stereoselective detection can be achieved by this methodology using chiral films on these substrates.[21]

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