

# Photoluminescent Properties of Cadmium Selenide Coated with a Photoactive Cobalt Coordination Complex: A Dioxygen-Driven Transducer

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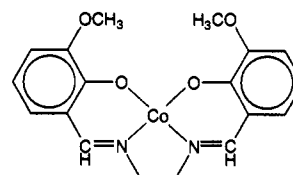
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**Abstract:** In methylene chloride solution, in the absence of dioxygen, addition of *N,N'*-ethylenebis(3-methoxysalicylideneiminato)cobalt(II), Co(3-MeO-salen), enhances the band gap photoluminescence (PL) intensity of etched, single-crystal n-CdSe relative to its intensity in methylene chloride alone, suggesting that the complex acts as a Lewis base toward the solid. Use of a dead-layer model permits an estimate of the maximum adduct-induced reduction in depletion width of  $\sim 130 \text{ \AA}$ . The PL enhancement is concentration dependent, saturating at  $\sim 40 \mu\text{M}$ , and can be well fit by the simple Langmuir adsorption isotherm model in this concentration regime, yielding an equilibrium constant  $K$  of  $\sim 10^4\text{--}10^5 \text{ M}^{-1}$ . At higher concentration, between  $\sim 50$  and  $100 \mu\text{M}$ , there is an irreversible, concentration-independent (to  $\sim 1000 \mu\text{M}$ ) inversion of the PL response to a net quenching, which is consistent with multilayer film formation. A thin layer of Co(3-MeO-salen) adsorbed onto CdSe from methylene chloride solution acts as a transducer: Exposure of the coated semiconductor to gaseous dioxygen quenches the band gap PL intensity relative to its intensity in a nitrogen atmosphere, while negligible PL intensity changes are induced by dioxygen in the absence of the film. The dioxygen-induced PL quenching is pressure-dependent; a good fit to the Langmuir model yields an equilibrium constant  $K$  of  $\sim 10$  to  $20 \text{ atm}^{-1}$ . The film is observed to be photoactive: Excitation at wavelengths shorter than  $\sim 600 \text{ nm}$ , which are absorbed by the oxygenated complex, induces the loss of dioxygen from the film, giving fractional quenching of PL intensity that increases with decreasing incident intensity. Implications for on-line sensor design using this transduction strategy are discussed.

## Introduction

In recent studies of gas-surface interface reactions, we have shown that the band gap photoluminescence (PL) intensity of single-crystal n-CdSe can be reversibly perturbed by surface adduct formation relative to the PL intensity in a reference ambient, typically nitrogen.<sup>1-3</sup> In many cases, these PL changes appear to be induced by expansions or contractions in the electric field present in the near-surface region of the solid (the depletion region), which are caused by adsorption of Lewis acids and bases, respectively. Despite our ability to detect in this way many classes of gaseous species, including, e.g., amines, butenes, and boranes, there are many other small molecules, including dioxygen, that do not elicit a significant PL response relative to a nitrogen reference ambient. A strategy for extending this methodology to embrace these species is to coat the semiconductor with a coordination complex that has a strong affinity for the surface and that can reversibly bind the targeted analyte to perturb the depletion region in the underlying semiconductor.

In this paper we demonstrate the viability of this approach using films of *N,N'*-ethylenebis(3-methoxysalicylideneiminato)cobalt(II), shown below and abbreviated as [Co(3-MeO-salen)]. This complex and several of its derivatives exhibit reversible dioxygen binding at room temperature in both the solid state and in solution.<sup>4-7</sup>



We show that this complex interacts strongly with the surface of CdSe in methylene chloride solution, both in the presence and absence of dioxygen in the solution. Films of Co(3-MeO-salen) on CdSe are readily prepared, and we report herein that these films lead to reversible dioxygen-induced quenching of PL intensity relative to a nitrogen reference ambient. Moreover, the film's photoreactivity can be used to enhance the rate of dioxygen desorption from the film.

## Experimental Section

**Materials.** Single-crystal, vapor-grown c-plates of n-CdSe, having a resistivity of about  $2 \text{ ohm}\cdot\text{cm}$ , were obtained from Cleveland Crystals, Inc. These crystals were etched in  $\text{Br}_2/\text{MeOH}$  (1:15 v/v), revealing the shiny Cd-rich (0001) face that was illuminated in these PL experiments. The oxygen gas was purchased from the Liquid Carbonic Specialty Gas Corporation (purity 99.6%). Methylene chloride (Aldrich; 99+% w/w) was distilled over calcium hydride under nitrogen. Both nitrogen and oxygen were delivered through drying tubes packed with anhydrous  $\text{CaCl}_2$  before exposure to the n-CdSe sample.

**Synthesis of [Co(3-MeO-salen)] $\cdot$ 2H $_2$ O.** The complex *N,N'*-ethylenebis(3-methoxysalicylideneiminato)cobalt(II) [Co(3-MeO-salen)] was prepared and isolated as the monohydrate, [Co(3-MeO-salen)] $\cdot$ H $_2$ O. In a typical synthesis, a 2.73-g quantity of 3-methoxysalicylaldehyde (Aldrich;

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(1) Meyer, G. J.; Lisensky, G. C.; Ellis, A. B. *J. Am. Chem. Soc.* **1988**, *110*, 4914.

(2) Meyer, G. J.; Leung, L. K.; Yu, J. C.; Lisensky, G. C.; Ellis, A. B. *J. Am. Chem. Soc.* **1989**, *111*, 5146.

(3) Neu, D. R.; Olson, J. A.; Ellis, A. B. *J. Phys. Chem.* **1993**, *97*, 5713.

(4) Paris, M. R.; Aymes, D. *Bull. Soc. Chim. Fr.* **1976**, 1431.

(5) Jones, R. D.; Summerville, D. A.; Basolo, F. *Chem. Rev.* **1979**, *79*, 139.

(6) (a) Calvin, M.; Barkelew, C. H. *J. Am. Chem. Soc.* **1946**, *68*, 2267.

(b) Hughes, E. W.; Wilmarth, W. K.; Calvin, M. *J. Am. Chem. Soc.* **1946**, *68*, 2273.

(7) Floriani, C.; Calderazzo, F. *J. Chem. Soc. (A)* **1969**, 946.

*o*-vanillin, 99%) is dissolved in 50 mL of absolute ethanol (Aaper) in a 250 mL Erlenmeyer flask. Addition of 0.50 mL of ethylenediamine (Baker) causes the yellow solution to turn orange, and a yellow precipitate forms. After addition of 7.5 g of sodium acetate trihydrate (EM), the solution is heated to reflux to yield the 3-methoxysalen ligand in solution. A solution of cobalt(II) is prepared by dissolving 1.88 g of cobalt diacetate tetrahydrate (Aldrich) in 25 mL of distilled water at room temperature. The pink cobalt(II) solution is added to the refluxing 3-methoxysalen ligand solution one dropper-full at a time; the ligand solution must be boiling vigorously during the entire addition, or the yield will be low. A dark red crystalline product forms. After cooling in an ice bath, the product is isolated by suction filtration and washed with small portions of water, ethanol, and diethyl ether. The yield is 90%. Elem. Anal. Calcd for the monohydrate,  $\text{CoC}_{18}\text{H}_{20}\text{N}_2\text{O}_5 \cdot \text{H}_2\text{O}$ : Co, 14.6; C, 53.6; N, 6.94; H, 5.01. Found: Co, 15.6; C, 53.0; N, 6.80; H, 4.95. Elemental analysis was performed at Galbraith Laboratories, Inc., Knoxville, TN. [ $\text{Co}(3\text{-MeO-salen})\text{H}_2\text{O}$ ] is a high spin complex, exhibiting a magnetic susceptibility,  $\mu$ , of  $4.3 \pm 0.1 \mu_B$  (Guoy method;  $\text{HgCo}(\text{SCN})_4$  standard) with three unpaired electrons by the spin-only approximation.

**Oxygen Reactivity of Solid [ $\text{Co}(3\text{-MeO-salen})\text{H}_2\text{O}$ ].** The Co atom in solid [ $\text{Co}(3\text{-MeO-salen})\text{H}_2\text{O}$ ] is five coordinate and does not react with oxygen. The water is removed by heating at 170 °C in vacuo (1 torr) to produce a dark brown, low-spin Co(II) product,  $\mu = 2.2 \pm 0.1 \mu_B$ , with one unpaired electron. Upon exposure to dioxygen gas, the mass of the dehydrated solid increases; the higher mass corresponds to addition of  $0.48 \pm 0.03$  mol  $\text{O}_2$  per mol Co and yields a diamagnetic product,  $\mu = 1.0 \pm 0.1 \mu_B$ . A weighed sample of the oxygenated solid was placed in a flask attached to a vacuum line, cooled to liquid nitrogen temperature and evacuated. As the sample warmed to room temperature,  $0.49 \pm 0.02$  mol  $\text{O}_2$  per mol Co were evolved, collected, and measured using a Toepler pump.

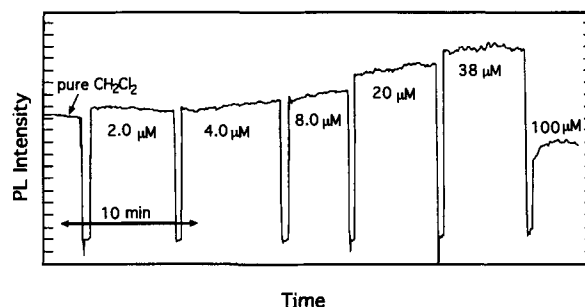
The photoreactivity of oxygenated  $\text{Co}(3\text{-MeO-salen})$  was confirmed by direct observation: A 0.12-g sample, dehydrated by heating in vacuo, was sealed in a glass bulb on a closed gas-handling system. By filling the system with 730 Torr dioxygen, the complex was oxygenated, with equilibrium reached within 15 min. When the solid was then irradiated with an expanded 458-nm laser line at an intensity of  $\sim 10 \text{ mW/cm}^2$ , the oxygen pressure in the system slowly increased from 713 to 716 Torr, presumably due to photoinduced desorption of dioxygen from the solid  $\text{Co}(3\text{-MeO-salen})$  sample. The bulb was bathed in a 5 L/min nitrogen flow to maintain constant temperature. Repeating the experiment with an argon-filled bulb yielded no pressure change, indicating that the gas temperature inside the bulb was not significantly increased on irradiation. Oxygen pressures inside the system were measured with an MKS Instruments Baratron capacitance manometer calibrated for 1–1000 Torr.

**Film Preparation.** Samples of [ $\text{Co}(3\text{-MeO-salen})\text{H}_2\text{O}$ ] are also dehydrated by dissolving the solid in an anhydrous solvent. For the gas-phase experiments, the anhydrous  $\text{Co}(3\text{-MeO-salen})$  film was deposited by dipping the CdSe sample in a 5 mM [ $\text{Co}(3\text{-MeO-salen})\text{H}_2\text{O}$ ] methylene chloride solution for 2 min, rinsing, and drying under a nitrogen stream. These coated samples showed reversible PL responses to dioxygen exposure. Use of crystallographic data permits an estimate of an upper limit on film thickness, assuming uniform coverage after evaporation of a drop of solution, of  $\sim 0.1 \mu\text{m}$ .<sup>8</sup>

**Apparatus.** The sample cell consisted of a glass tube of 20-mm inner diameter with a sidearm inlet. A valve with a Teflon stopcock was also added at the base of the tube. The semiconductor sample was mounted with Teflon supports or Duco adhesive on a glass rod in the center of the tube. Nitrogen–oxygen mixtures were prepared by mixing metered gas flows, measured with Gilmont floating ball-type flow meters calibrated for 0–10 and 0–100 mL/min of air flow, with corrections made for the viscosities of pure nitrogen and oxygen.

**Optical Measurements.** Electronic absorption spectra were obtained with a Cary 17D spectrophotometer. For PL measurements, a Coherent Innova 90-5 3.0-W  $\text{Ar}^+$  laser was used for 458-, 476-, 496-, and 514-nm excitation; and a Melles-Griot Model 80 10-mW HeNe laser or a Spectra-Physics 40-mW HeNe laser provided 633-nm ultraband gap excitation. Photoluminescence data were collected with 512- or 1024-element, computer-interfaced Oriol Instaspec II systems. Laser light intensities were measured with a Coherent Model 212 power meter.

For solution-phase experiments, the red band-edge PL of n-CdSe was monitored at the band maximum of  $\sim 720 \text{ nm}$ , while the n-CdSe sample was immersed in pure methylene chloride solvent or in a [ $\text{Co}(3\text{-MeO-salen})\text{H}_2\text{O}$ ] methylene chloride solution. Changes in the liquid ambient were carried out by draining the liquid through the Teflon stopcock and injecting a new solution or pure solvent via syringe through the sidearm inlet. A nitrogen-filled bag was kept over the sidearm.



**Figure 1.** The PL intensity of an etched n-CdSe sample during exposure to pure  $\text{CH}_2\text{Cl}_2$  (initial intensity) and to increasing concentrations of deoxygenated [ $\text{Co}(3\text{-MeO-salen})\text{H}_2\text{O}$ ]  $\text{CH}_2\text{Cl}_2$  solutions. The PL was excited by 633-nm light ( $\sim 40 \text{ mW/cm}^2$ ) and monitored at 720 nm. The PL enhancement maximizes at  $\sim 40 \mu\text{M}$  with signature inversion (PL quenching relative to the reference level) occurring above  $\sim 50 \mu\text{M}$ , as seen for the last addition (right side). The vertical spikes correspond to changes in the liquid ambient. The bottom of the figure corresponds to zero light intensity.

For the gas-phase experiments, the coated semiconductor sample was mounted in the cell and its band-edge PL was monitored with the sample under 1 atm of dry nitrogen, oxygen, or a metered mixture of the two gases. The test gas was introduced via the sidearm inlet at a total flow rate of 100 mL/min.

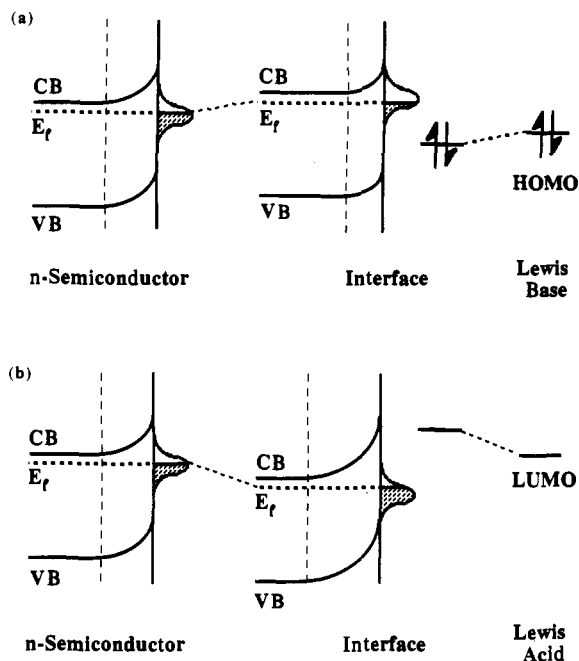
## Results and Discussion

**Solution Studies under Nitrogen.** Samples of etched, single-crystal n-CdSe emit red band-edge PL when excited with ultraband gap light (the band gap energy,  $E_g$ , is  $\sim 1.7 \text{ eV}$ ;  $\lambda_{\text{max}} \sim 720 \text{ nm}$ ). When the liquid ambient surrounding the n-CdSe sample is switched from pure methylene chloride to a deoxygenated methylene chloride solution of  $\text{Co}(3\text{-MeO-salen})\text{H}_2\text{O}$ , of concentration less than  $\sim 50 \mu\text{M}$ , the intensity of the band-edge PL is reversibly enhanced, as shown in Figure 1; because the PL spectral distribution at low resolution ( $\sim 0.5 \text{ nm}$ ) was unaffected by adsorption, PL intensity changes were monitored exclusively at the band maximum. We presume the dominant reactive species in this solution is the coordinatively unsaturated  $\text{Co}(3\text{-MeO-salen})$ .

We have interpreted the PL enhancement as arising from a charge-transfer complex with a Lewis base;<sup>3</sup> a possible binding scenario might be that the oxygen atoms of the anionic ligand serve as electron donors to surface Cd sites. Adsorption by a Lewis basic species can shift the distribution of electrons between the bulk of the semiconductor and its surface states, thereby causing changes in PL intensity: As shown on the left-hand side of Figure 2a, prior to adsorption, coordinatively unsaturated surface atoms can give rise to intraband gap surface electronic states that are filled to the Fermi level with electrons from the bulk of the solid. This creates a depletion region near the surface, which is expected to be largely nonemissive, since photogenerated electron-hole pairs are swept apart by the electric field in this region and prevented from recombining.

Interaction of the surface states with the highest occupied molecular orbital (HOMO) of an adsorbing Lewis base destabilizes the surface states, moving them closer in energy to the conduction band edge. The surface states now can accommodate fewer electrons, and some electrons previously trapped at the surface return to the bulk of the solid. This reduces the depletion region (and nonemissive zone), and PL intensity relative to a reference ambient is enhanced, center of Figure 2a. For  $\text{Co}(3\text{-MeO-salen})$  in deoxygenated  $\text{CH}_2\text{Cl}_2$ , the PL enhancement saturates at an ambient cobalt complex concentration of  $\sim 40 \mu\text{M}$ .

In the cobalt complex concentration range of  $\sim 50$  to  $100 \mu\text{M}$ , a remarkable *irreversible* inversion of the PL signature occurs, Figure 1, and net quenching is seen relative to the reference PL level; the magnitude of the quenching, typically  $\sim 20\%$  relative



**Figure 2.** Molecular orbital diagrams for perturbation of the electronic structure of a semiconductor contacting a nonelectrolyte liquid phase by adsorption of (a) a Lewis base and (b) a Lewis acid. The left-hand sides of (a) and (b) show the electronic structure of the solid prior to adsorption, including a hypothetical surface state distribution. Interaction of the surface states with the HOMO of a Lewis base (a) stabilizes the HOMO and destabilizes the surface states, moving them closer to the conduction band edge; this causes electrons to return to the bulk and decreases the depletion region (center part of the figure). Conversely, interaction of the surface states with the LUMO of a Lewis acid (b) destabilizes the LUMO and stabilizes the surface states, moving them closer to the valence band edge; this brings more electrons from the semiconductor bulk to occupy the surface states and increases the depletion region (center part of the figure). Vertical dashed lines indicate the approximate extent of the depletion width.

to the reference level with 633-nm excitation, is independent of concentration up to  $\sim 1000 \mu\text{M}$ . This inversion of the PL signature was reproducible in three separate runs, with the crystal re-etched between runs. The characteristics of the PL quenching—its abrupt onset over a narrow concentration regime, the insensitivity of PL intensity to further increases in concentration, and the inability to reverse the effect with repeated solvent washings—are all consistent with multilayer film formation. PL quenching can be viewed as arising from a surface interaction in which the adsorbate acts as a Lewis acid, stabilizing the surface states by interaction with its lowest unoccupied molecular orbital (LUMO), as shown in Figure 2b. Net electron withdrawal could occur during the proposed incipient film formation by, for example, use of different binding sites, changes in ligation (binding of Co atoms to Se surface atoms, e.g.), and aggregation-induced electronic effects.

**Dead-Layer Model.** The amount of PL enhancement at low Co complex concentrations can be treated quantitatively using a so-called dead-layer model, wherein the near-surface region of thickness on the order of the depletion width is assumed to be a nonemissive layer, or dead-layer. The quantitative form of the dead-layer model is given by eq 1<sup>9,10</sup>

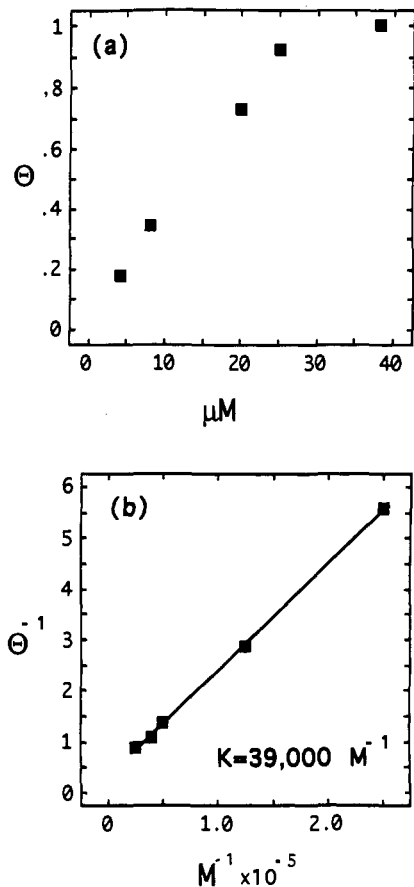
$$\text{PL}_{\text{ref}}/\text{PL}_x = \exp(-\alpha'\Delta D) \quad (1)$$

where  $\text{PL}_{\text{ref}}$  is the PL intensity in the reference ambient;  $\text{PL}_x$  is

(8) Calligaris, M.; Nardin, G.; Randaccio, L. *J. Chem. Soc., Dalton Trans.* 1974, 1903.

(9) Burk, A. A., Jr.; Johnson, P. B.; Hobson, W. S.; Ellis, A. B. *J. Appl. Phys.* 1986, 59, 1621.

(10) Mettler, K. *J. Appl. Phys.* 1977, 12, 75.



**Figure 3.** (a) Plot of fractional surface coverage  $\Theta$  vs Co(3-MeO-salen) concentration in  $\text{CH}_2\text{Cl}_2$  solution. (b) Double-reciprocal plot of the same data; the linearity of the plot (correlation coefficient of 0.99) represents a good fit to the Langmuir adsorption isotherm model, and the reciprocal of the slope yields an equilibrium constant  $K$  of  $39,000 \pm 1000 \text{ M}^{-1}$ .

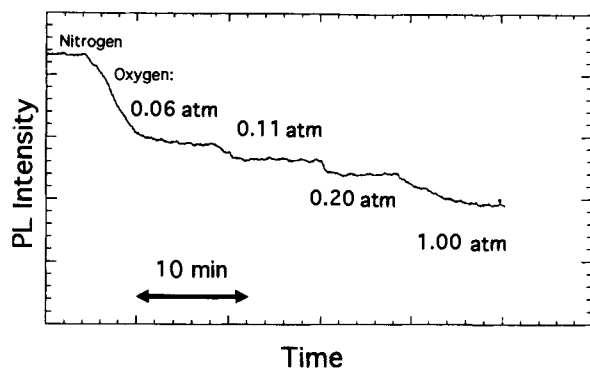
the PL intensity in the presence of the adsorbing species;  $\alpha' = (\alpha + \beta)$  is the sum of the semiconductor absorptivities for exciting and emitted light; and  $\Delta D = (D_{\text{ref}} - D_x)$  is the reduction in dead-layer thickness accompanying adsorption of the Lewis base. In using eq 1, we assume that the surface recombination velocity  $S$  either is unaffected by adduct formation or is very large ( $S \gg L/\tau$  and  $S \gg \alpha L^2/\tau$ , where  $L$  and  $\tau$  are the minority carrier diffusion length and lifetime, respectively), both in the absence and presence of the adsorbate.<sup>9</sup>

Values of  $\Delta D$  derived from PL experiments are independent of excitation wavelength (458, 514, and 633 nm) in agreement with the dead-layer model. At  $\sim 50 \mu\text{M}$  concentration of the cobalt complex, the PL enhancement has saturated, corresponding to a maximum contraction in the dead-layer thickness of  $\sim 130 \pm 20 \text{ \AA}$ .

**Langmuir Adsorption Isotherm Model.** The concentration dependence of the PL enhancement can be used to estimate the equilibrium constant for adduct formation through the use of the Langmuir adsorption isotherm model. The quantitative form of this model is given by eq 2<sup>11</sup>

$$\Theta = KC/(1 + KC) \quad \text{or} \quad 1/\Theta = 1 + (1/KC) \quad (2)$$

where  $\Theta$  is the fractional surface coverage for active binding sites;  $K$  is the equilibrium constant for adduct formation, and  $C$  is the concentration of the uncomplexed species. Values of  $\Theta$  are estimated as the fractional PL changes occurring between the reference ambient ( $\Theta = 0$ ) and saturated PL enhancement ( $\Theta = 1$ ), which, as noted above, is assumed to correspond to completion of an initial stage of coverage that precedes the multilayer coverage



**Figure 4.** Changes in the PL intensity of a Co(3-MeO-salen)-coated n-CdSe sample as a function of oxygen partial pressure. The reference level is pure nitrogen. The gaseous ambient is switched from nitrogen to metered mixtures of nitrogen and oxygen at 1 atm and 100 mL/min flow rate. The PL was excited by 633-nm light ( $\sim 40$  mW/cm<sup>2</sup>) and monitored at 720 nm. The bottom of the figure corresponds to zero light intensity.

proposed to correspond to PL quenching at high concentrations of the Co complex.

Figure 3 shows representative data for the adsorption of Co(3-MeO-salen) in the absence of dioxygen onto the (0001) face of etched n-CdSe. Good fits to the model obtain, and binding constants  $K$  of  $\sim 10^4$ – $10^5$  M<sup>-1</sup> are found for a variety of CdSe samples.

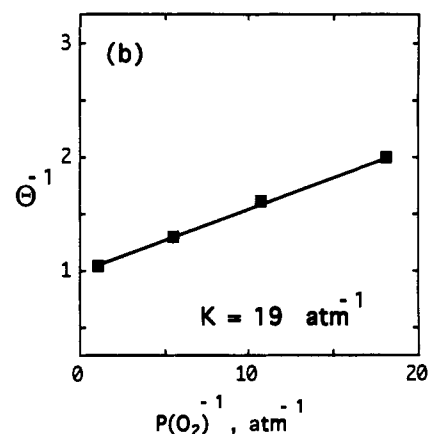
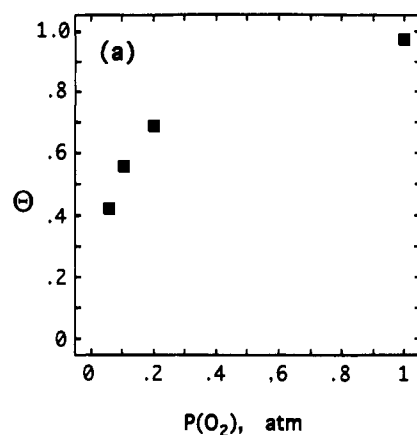
**Oxygenated Solutions.** The reference PL intensity level in methylene chloride is unchanged between nitrogen- and oxygen-saturated solvent. However, oxygenated (1 atm O<sub>2</sub>) methylene chloride solutions of Co(3-MeO-salen) gave dramatically different PL results than the deoxygenated solutions discussed above.

In solution Co(3-MeO-salen) reacts with dioxygen to form either a simple adduct, Co(3-MeO-salen)O<sub>2</sub>, a dioxygen-bridged dimer, Co(3-MeO-salen)-O<sub>2</sub>-Co(3-MeO-salen), or a mixture of both, depending on the choice of solvent and the presence of other potential axial ligands.<sup>7</sup> We find that in the presence of oxygen, whatever Co(3-MeO-salen)-derived species are present appear to act as Lewis acids toward the surface, quenching PL intensity relative to a methylene chloride ambient, perhaps reflecting ligation in which Co is bonded to surface Se atoms. Previously reported X-ray PES studies indicate that both [Co(3-MeO-salen)-O<sub>2</sub>-Co(3-MeO-salen)] and (O<sub>2</sub>)Co(3-MeO-salen)(pyridine) have Co binding energies characteristic of Co(III);<sup>12</sup> and their larger values relative to Co(3-MeO-salen), a Co(II) complex, are consistent with enhanced Lewis acidity.

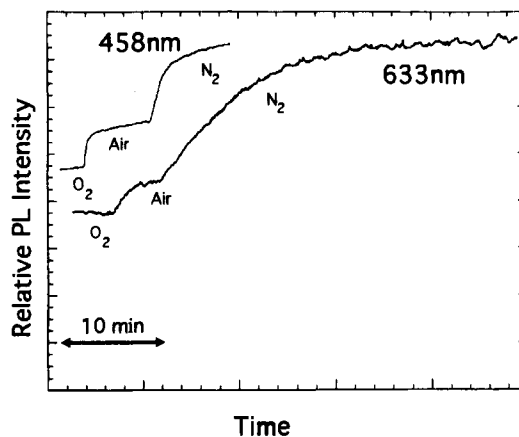
Concentration studies conducted to obtain binding constants yielded very poor fits to eq 2. The dissociative Langmuir adsorption isotherm model for two-site adsorption with dissociation<sup>11</sup> likewise yielded an unsatisfactory fit, and no further studies were conducted on this system.

**Coatings.** In the solid state, [Co(3-MeO-salen)]H<sub>2</sub>O is a high-spin Co(II) complex with three unpaired electrons that is unreactive toward dioxygen. Dehydration of the solid by heating in vacuo produces a low-spin Co(II) complex with one unpaired electron. The dehydrated bulk solid reacts reversibly with dioxygen to yield Co(3-MeO-salen)-O<sub>2</sub>-Co(3-MeO-salen), which is diamagnetic. Similar reactivity has been reported for other Co(salen) derivatives.<sup>5,6,13</sup>

Samples of [Co(3-MeO-salen)]H<sub>2</sub>O can also be dehydrated by dissolving the solid in an anhydrous solvent. Dipping the n-CdSe sample in oxygen-free 5 mM [Co(3-MeO-salen)]H<sub>2</sub>O



**Figure 5.** (a) Fractional surface coverage  $\Theta$  vs dioxygen partial pressure. (b) Double-reciprocal plot of the same data; the linearity of the plot (correlation coefficient of 0.99) represents a good fit to the Langmuir adsorption isotherm model, and the reciprocal of the slope yields an equilibrium constant  $K$  of  $19 \pm 1$  atm<sup>-1</sup>.



**Figure 6.** Excitation wavelength dependence of the dioxygen-induced PL response: Note the larger fractional response but more sluggish return to nitrogen atmosphere baseline for 633-nm, red light, compared to the faster response with 458-nm, blue light. The excitation intensity is 160 mW/cm<sup>2</sup> in both experiments, with the traces normalized to the same intensity in the nitrogen atmosphere. The bottom of the figure corresponds to zero light intensity.

methylene chloride solution leaves a thin film of the anhydrous Co(3-MeO-salen) complex on the sample surface upon evaporation of the solvent under a nitrogen stream. While no PL response is observed on exposure of uncoated CdSe crystals to dioxygen, when the gaseous ambient is switched from nitrogen at 1 atm and 100 mL/min flow rate to metered mixtures of dry nitrogen and oxygen at the same flow rate, the PL intensity of the coated

(11) Atkins, P. W. *Physical Chemistry*, 4th ed.; W. H. Freeman and Co.: New York, NY, 1990; pp 885–888.

(12) Burness, J. H.; Dillard, J. G.; Taylor, L. T. *J. Am. Chem. Soc.* **1975**, *97*, 6080.

(13) Earnshaw, A.; Hewlett, P. C.; King, E. A.; Larkworthy, L. F. *J. Chem. Soc. (A)* **1968**, 241.

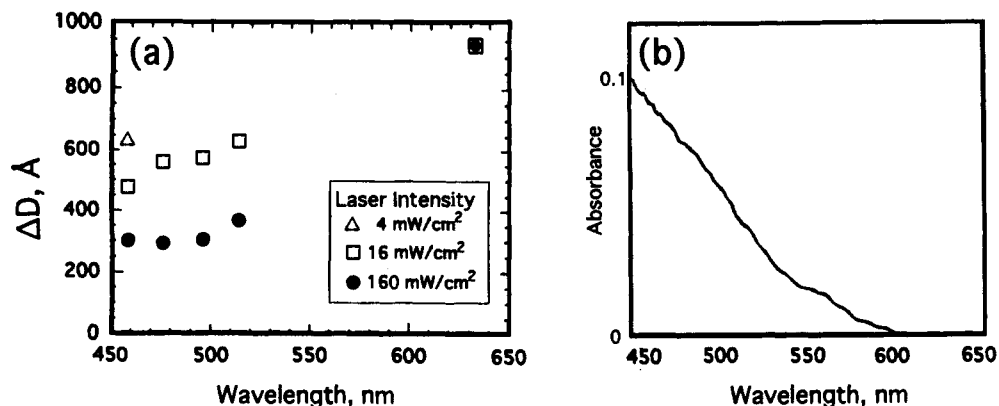


Figure 7. (a) Values of  $\Delta D$  calculated using eq 1 for the exposure of a Co(3-MeO-salen)-coated n-CdSe sample to dioxygen at 1 atm and 100 mL/min flow rate. The same sensor structure was cycled between nitrogen and oxygen at the various indicated excitation wavelengths and intensities. (b) Absorption spectrum for an oxygenated (under 1 atm O<sub>2</sub>) Co(3-MeO-salen) film deposited on a quartz slide from CH<sub>2</sub>Cl<sub>2</sub> solution.

samples is reversibly quenched, as shown in Figure 4, consistent with producing surface-proximate Lewis acidic Co(III) sites.

The concentration dependence of the PL intensity changes can be used to estimate the equilibrium binding constant, using the aforementioned Langmuir adsorption isotherm model. Figure 5 illustrates the good fit obtained, which yields an equilibrium constant  $K$  of  $19 \pm 1$  atm<sup>-1</sup>. The threshold pressure for obtaining a PL response is typically on the order of 0.01 atm; and saturation of the PL changes occurs in the vicinity of 1 atm dioxygen pressure. Experiments on a variety of coated samples yield dioxygen binding constants  $K$  of  $\sim 10$ – $20$  atm<sup>-1</sup>; these values are in the range estimated for the oxygenation of bulk Co(3-MeO-salen) samples.<sup>6b</sup>

**Film Photoeffects on Dead-Layer Thickness.** The dead-layer model agreement observed for Co(3-MeO-salen) adsorption onto CdSe in deoxygenated solution was not found for the PL response of the coated sample to dioxygen. Rather,  $\Delta D$  values decreased substantially with decreasing excitation wavelength when a common excitation intensity of  $\sim 16$  mW/cm<sup>2</sup> was employed:  $\Delta D$  values decreased from  $\sim 1000$  Å for 633-nm excitation down to  $\sim 500$  Å with 458-nm excitation. However, the raw data corresponding to this experiment showed an unusual kinetic feature. Figure 6 shows PL traces obtained with 633- and 458-nm excitation. Especially noteworthy is the much faster return to nitrogen atmosphere PL intensity baseline obtained with 458-nm light. As we would not expect the kinetics of desorption for an uncoated surface to depend on the interrogating wavelength, this result suggests that the film is photoactive.

The absorption spectrum of an oxygenated Co(3-MeO-salen) film (under 1 atm O<sub>2</sub>) was obtained on a quartz slide, Figure 7b, and indicates that the film is essentially transparent at 633 nm but displays some absorption at 514 nm and greater absorption at 458 nm. The PL signatures and calculated dead-layer values are consistent with the notion that photolysis of the oxygenated film is occurring, driving dioxygen out of the coating. To test this hypothesis, we repeated the PL experiments with lower incident intensities, which would permit larger steady-state concentrations of adsorbed dioxygen, if photoinduced desorption of dioxygen were occurring. As Figure 7a illustrates, there is no effect on the  $\Delta D$  value obtained with 633-nm excitation, where the film is transparent; but  $\Delta D$  values rise considerably (cor-

responding to enhanced PL quenching) with shorter excitation wavelengths as the incident intensity declines, and increasingly satisfactory agreement with the dead-layer model— $\Delta D$  values that are more nearly independent of excitation wavelength—is observed.

Photoinduced loss of dioxygen was also observable from direct photolysis of a powdered sample of Co(3-MeO-salen) with 458-nm light, as described in the Experimental Section.

**Sensor Considerations.** The response of Co(3-MeO-salen)-coated CdSe to dioxygen demonstrates that analytes not detectable on etched CdSe surfaces can nonetheless be detected by coupling the response to a film possessing the desired chemical reactivity. The sensitivity in this case extends down only to  $\sim 0.01$  atm; however, films having higher binding constants may be used to extend the limits of detection, although they may not have the ease of reversibility found with this structure.

The effect of water on this structure is also noteworthy: Water vapor initially enhances the PL intensity, but prolonged exposure leads to irreversible loss of PL intensity, presumably due to photoassisted decomposition of CdSe. However, simply storing the coated sample in a humid atmosphere causes no loss of response to dry dioxygen. Indeed, these structures appear to be considerably more robust than the uncoated semiconductors we have previously studied; Whereas we normally find that n-CdSe samples must be regularly re-etched, even when stored under nitrogen, samples with adsorbed Co(3-MeO-salen) films have continued to show reversible, undegraded PL responses to dry dioxygen in oxygen–nitrogen cycling experiments after more than six weeks of storage in humid air. Additional experiments with metal complex-coated, semiconductor structures are presently underway in our laboratories.

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