

Photoluminescent Properties of Cadmium Selenide in Contact with Solutions and Films of Metalloporphyrins. Evidence for Semiconductor-Mediated Adduct Formation of Oxygen with Metalloporphyrins at Room Temperature

Albena Ivanisevic and Arthur B. Ellis*

Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706

Received: August 21, 1998; In Final Form: December 10, 1998

The band-edge photoluminescence (PL) intensity of etched n-CdSe single crystals is modulated through adsorption of 17 porphyrins and metalloporphyrins from methylene chloride solution. In nitrogen-saturated solution, the PL intensity is reversibly enhanced through adduct formation with octaethylporphyrin (OEP), tetraphenylporphyrin (TPP), their divalent Co, Cu, and Cd derivatives, and with tetra(pentafluorophenyl)porphyrin (TFP), tetra-(4-tolyl)porphyrin (TTP), and tetra-(4-pyridyl)porphyrin (TPyP); in contrast, the PL intensity is reversibly quenched by exposure to divalent Mg, Ni, and Zn complexes of OEP and TPP. The concentration dependence of the PL changes can be fit to the Langmuir adsorption isotherm model to yield binding constants that range from $\sim 10^3$ to 10^5 M⁻¹. Saturating methylene chloride with oxygen rather than nitrogen does not affect the CdSe PL nor does oxygen affect the (metallo)porphyrin absorption spectra in methylene chloride solution. However, many of the metalloporphyrin-induced PL responses and binding constants are substantially affected by the change in dissolved gas ambient, evidencing surface-mediated adduct formation between oxygen and these metalloporphyrins at room temperature. Particularly large effects are observed for the Mg, Ni, and Zn OEP and TPP complexes, which produce PL enhancements in oxygen-saturated solution rather than PL quenching in nitrogen-saturated solution. When a thin film of each metalloporphyrin is deposited onto CdSe substrates by solvent evaporation, oxygen can be detected through reversible PL enhancement (NiTPP and ZnTPP) or quenching (all other metalloporphyrins examined save for CdOEP and CdTPP, which gave no response) relative to a gaseous nitrogen ambient. Binding constants obtained were typically in the range ~ 1 – 10 atm⁻¹. Steric and electronic contributions to these effects are discussed.

Introduction

In previous studies we and others have shown that the band-edge photoluminescence (PL) intensity of single crystal n-CdSe samples and other emissive semiconductors can be reversibly altered as a result of the introduction of a number of species in solution and gaseous ambients, representing a form of on-line chemical sensing.¹ In some cases we have been able to detect molecules that do not elicit a PL response relative to a reference ambient by coating the surface of the solid with a transducing film that has specific reactivity toward the analyte of interest and that couples electronically with the semiconductor to produce a change in PL intensity. Prototypical examples have been films of Vaska's complex, *trans*-IrCl(CO)(PPh₃)₂, and the Schiff base complex [Co(3-MeO-salen)], films that signal the presence of oxygen relative to nitrogen by causing quenching of the substrate CdSe PL intensity.²

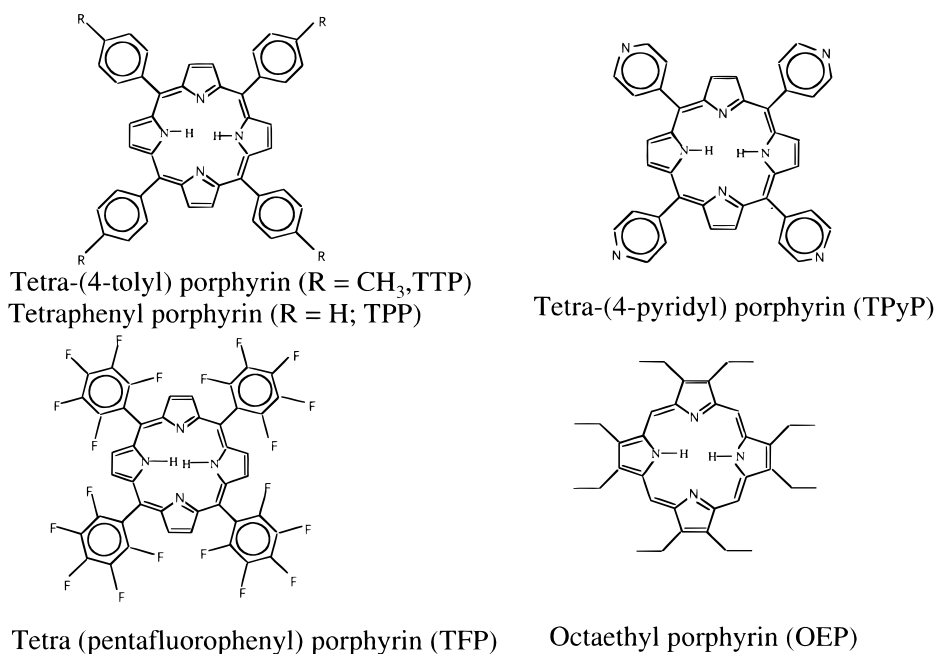
Our results with the Schiff base complex prompted us to explore the interaction of (metallo)porphyrins with single-crystal CdSe substrates in the presence and absence of oxygen. Recent literature on (metallo)porphyrins is vast and highlights the critically important role that these compounds play in many biological systems.³ Reversible adduct formation of some metalloporphyrins with oxygen is a particularly important reaction that in many cases cannot be studied at room temperature, owing to the weakness of the interaction between the

reaction partners. Some examples involving characterization of Fe porphyrin–oxygen adducts at low temperature have been reported in solution and on silica supports.^{4,5} In principle, emissive semiconductor substrates could provide a probe for such complexation phenomena. That metalloporphyrins can strongly bind to such surfaces has been demonstrated through use of nonstoichiometric CdS clusters whose PL intensity was irreversibly quenched by adsorption of metalloporphyrins from 2-propanol solution.^{6,7}

In this paper we use single-crystal n-CdSe substrates to examine adsorption-induced PL changes in methylene chloride solution from tetra-(4-tolyl)porphyrin (TTP), tetra-(4-pyridyl)porphyrin (TPyP), tetra(pentafluorophenyl)porphyrin (TFP), octaethylporphyrin (OEP), and tetraphenylporphyrin (TPP), whose structures are shown in Chart 1, and from the divalent Mg, Co, Ni, Cu, Zn, and Cd derivatives of OEP and TPP. We demonstrate that these compounds produce a rich set of PL responses in nitrogen-saturated solutions, with the magnitude and direction of the effect dependent on the choice of metal and ligand. Furthermore, many of the PL effects involving the metal complexes are greatly affected by the presence of dissolved oxygen, evidencing oxygen–metalloporphyrin adduct formation mediated by the semiconductor surface at room temperature. The sensitivity to oxygen is also reflected in the use of the metalloporphyrins as transducer films for CdSe substrates; reversible PL responses to oxygen are found relative to a nitrogen reference ambient.

* To whom correspondence should be addressed.

CHART 1



Experimental Section

Materials and Sample Preparation. Samples of MgTPP, CdTPP, and CdOEP were purchased from Porphyrin Products, UT, and the rest of the compounds in Chart 1 were obtained from Aldrich and used without further purification. Oxygen gas was obtained from Liquid Carbonic Specialty Gas Corporation and used as received. Methylene chloride (Aldrich, 99+%) was distilled from calcium hydride under nitrogen. Single-crystal, vapor-grown *c*-plates of n-CdSe, having a resistivity of $\sim 2 \Omega \text{ cm}$, were obtained from Cleveland Crystals, Inc. Prior to a PL experiment the crystals were etched in Br_2/MeOH (1:15 v/v), allowing the shiny Cd-rich (0001) face to be revealed and later illuminated in the PL experiment. Dry nitrogen or oxygen was bubbled through each solution for at least 5 min prior to each experiment. Flow meters were used to introduce variable percentages of each gas into the solution mixture.^{2a}

Films of each (metallo)porphyrin were prepared from 350–400 μM CH_2Cl_2 solutions. The CdSe sample was given a second etch in a solution of concentrated HCl, rinsed with methanol, and then dried in flowing nitrogen. Immediately after drying, two drops of the (metallo)porphyrin solution were spread on the crystal surface and the solvent allowed to evaporate.

Apparatus. A gas flow apparatus was assembled using Tygon tubing that allowed mixtures of nitrogen and oxygen to flow over the semiconductor surface while the solid was illuminated. Partial pressures of the gases were controlled by adjusting the flow rates of the incoming gases.^{2a} The total gas flow rates varied from 80 to 120 mL/min, and the total gas pressure was 1 atm.

The sample of CdSe was mounted on a glass rod between two Teflon rings within a glass cell.⁸ The cell was equipped with a sidearm, through which either solutions or gases could be introduced without disturbing the optical alignment.^{2a}

Optical Measurements. A Spectra-Physics He–Ne laser (632.8 nm) provided excitation of the semiconductor. Incident intensities ranged from 5 to 20 mW/cm^2 . Emission spectra were monitored using an Oriel Instaspec II silicon diode array spectrophotometer or Oriel Instaspec IV CCD spectrophotometer. A cutoff filter was used in the spectrophotometer to

permit collection of the band-edge PL at $\lambda_{\text{max}} \approx 720 \text{ nm}$ ($E_g \approx 1.7 \text{ eV}$). The entire PL spectrum was monitored, while tracking the PL intensity at a particular wavelength, typically the band maximum, as a function of time; the band maximum did not shift under the low-resolution (0.5 nm) spectral conditions employed. The signal collected was used for computer analysis utilizing InstaSpec1.1 for Windows 95. The solution UV–vis spectrum of each (metallo)porphyrin was obtained from a Hewlett-Packard HP89530A spectrophotometer at room temperature between 300 and 800 nm. The spectra of all compounds of this study had negligible absorbance at the 633 nm excitation and 720 nm emission wavelengths.

Results and Discussion

All 17 (metallo)porphyrins shown in Table 1 produced reversible responses in CdSe band-edge PL intensity ($\lambda_{\text{max}} \approx 720 \text{ nm}$) when adsorbed from a nitrogen- or oxygen-saturated methylene chloride solution onto the shiny (0001) face of the semiconductor. In sections below we discuss the PL changes accompanying adsorption of each compound onto CdSe, first in nitrogen-saturated solution and then in oxygen-saturated solution. The concentration dependence of the PL response is used to estimate equilibrium binding constants in both of the dissolved gas ambients. We describe the use of films of some of these compounds as transducers that produce an oxygen-driven PL response from the CdSe substrate relative to a nitrogen ambient. Finally, we discuss steric and electronic interactions that might account for some of the observed PL effects.

Nitrogen-Saturated Solution Studies. Porphyrins. A typical PL trace is displayed in Figure 1A, which reveals that addition of TPP to nitrogen-saturated methylene chloride solution begins to enhance CdSe PL intensity at about 20–50 μM and that the enhancement saturates at about 400 μM . The effect is seen to be readily reversible, with a return to solvent restoring the original PL intensity. Qualitatively, our prior studies have interpreted the enhancement of PL intensity as caused by the adsorption of a Lewis base onto the CdSe surface, which is accompanied by the formation of a weak charge-transfer complex between the absorbate and the CdSe surface atoms.^{1,2}

TABLE 1: PL Ratios and Binding Constants in Solution

compound	PL ratio ^a	K (M ⁻¹) ^b	PL ratio ^c	K (M ⁻¹) ^d
tetra-(4-tolyl)porphyrin (TTP)	5.30	2000	4.90	3000
tetra-(4-pyridyl)porphyrin (TPyP)	2.28	6000	2.20	2000
tetraphenylporphyrin (TPP)	4.83	3000	4.80	2000
octaethylporphyrin (OEP)	1.43	4000	1.42	6000
tetra (pentafluorophenyl)porphyrin ^e (TFP)	1.45	2000	1.46	2000
Mg(II) TPP	0.32	1000	1.60	3000
Co(II) TPP	1.73	40000	1.23	5000
Ni(II) TPP	0.80	4000	1.51	2000
Cu(II) TPP	1.26	4000	1.23	1000
Zn(II) TPP	0.33	50000	1.62	13000
Cd(II) TPP	1.22	2000	1.30	2000
Mg(II) OEP	0.76	11000	1.21	2000
Co(II) OEP	1.20	4000	1.19	5000
Ni(II) OEP	0.28	200000	1.38	10000
Cu(II) OEP	1.42	15000	1.25	19000
Zn(II) OEP	0.80	50000	1.25	6000
Cd(II) OEP	1.35	3000	1.48	3000

^a The ratio of CdSe PL intensity upon addition of the indicated compound to N₂-saturated CH₂Cl₂ solution (when PL changes were saturated with adsorbate concentration) relative to the PL intensity in N₂-saturated CH₂Cl₂ solvent. All data were collected on the same CdSe surface except where otherwise noted. The excitation wavelength was 633 nm, and PL intensity was measured at 720 nm. The error in a single measurement was less than 5%. ^b Equilibrium binding constants for adsorption of the indicated compound in nitrogen-saturated CH₂Cl₂ solution onto CdSe, obtained from fits to the Langmuir adsorption isotherm model, eq 2. The error in the Langmuir fit was generally less than 10%. ^c PL ratio as defined in footnote a, except that all data were obtained with O₂-saturated CH₂Cl₂ solutions. ^d Equilibrium binding constants as described in footnote b, except that all data were obtained with O₂-saturated CH₂Cl₂ solutions. ^e A different surface of a CdSe crystal was used for the investigation of this compound; OEP gave a similar response on this surface.

The mechanism underlying this effect is believed to be that 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 CdSe. The electron density that is donated from an adsorbed Lewis base can cause electrons trapped at the surface to move back into the bulk and, in an unpinned system, decrease the width of the surface depletion region. If this region is assumed to be nonemissive, because of the fact that electron-hole pairs created by the exciting light will be swept apart by the electric field present and prevented from recombining, adsorption of a Lewis base is expected to enhance the PL intensity by reducing the depletion width (changes in surface recombination velocity due to the adsorbate can also contribute to the observed PL changes.). The π system of the porphyrin is an accessible source of electron density for the semiconductor surface.⁹

For many adsorbate systems we have been able to treat the nonemissive region quantitatively as being a "dead layer" whose thickness is on the order of the depletion width.^{1,2} Use of different excitation wavelengths with different optical penetration depths revealed PL intensities in the reference (solvent) ambient and adsorbate-containing (solution) ambient whose ratio was in accord with this dead layer model. The intense absorption of the (metallo)porphyrins precludes a quantitative test of the dead layer model in these systems, but if electric field effects are driving the observed PL change, they are consistent with a net transfer of electron density from the porphyrin to the surface. A PL enhancement is found for all of the porphyrins of Chart 1.

The PL enhancement ratios relative to solvent that the porphyrins induce, observed in response to 633 nm excitation where the solutions are essentially transparent, are summarized

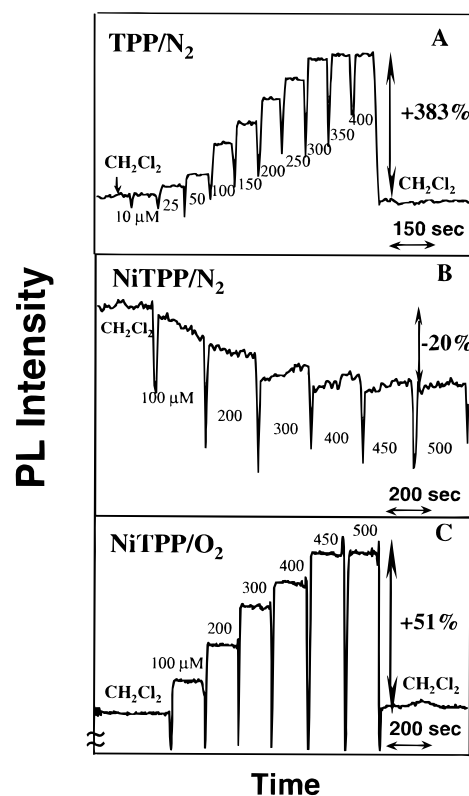


Figure 1. Changes in PL intensity of an etched n-CdSe crystal resulting from exposure to (A) TPP dissolved in N₂-saturated CH₂Cl₂, (B) NiTPP dissolved in N₂-saturated CH₂Cl₂, and (C) NiTPP dissolved in O₂-saturated CH₂Cl₂. The PL was excited in each case with 633 nm light and monitored at 720 nm. The downward spikes result from draining the sample cell when changing solutions.

in Table 1. The order seen is TFP \sim OEP $<$ TPyP $<$ TPP \sim TTP. The donor strength of the porphyrin is directly dependent on the presence of electron-donating or -withdrawing groups on the porphyrin ring. We would expect, for example, that the fluorinated porphyrin would be more electron-withdrawing than TPP and that OEP would be more electron-donating than TPP. The striking deviation of PL responses from this ordering suggests that steric effects may play an important role in adsorption. Assessing the relative importance of steric and electronic effects is complicated because these PL experiments do not enable us to compare absolute coverages, binding sites, or ligation geometries. In this context, it should be kept in mind that the etched surfaces employed in this study may contain, for example, impurity atoms or oxide phases and that they are topographically heterogeneous.

Metalloporphyrins. When the Mg, Co, Ni, Cu, Zn, and Cd TPP and OEP complexes were adsorbed onto CdSe, metal- and ligand-dependent PL responses were observed, as summarized in Table 1. Specifically, for both series of complexes, the Co, Cu, and Cd compounds caused enhancements with the effect much smaller in the metallo-TPP complexes than was found for TPP itself and about the same magnitude in the metallo-OEP complexes as was found for OEP. Interestingly, the relative magnitude of the effect changes among this trio in passing from the TPP to the OEP complexes: CdTPP \sim CuTPP $<$ CoTPP, but CoOEP $<$ CdOEP \sim CuOEP when the effects are examined on the same CdSe surface.

Most striking, however, was the substantial quenching observed for the Mg, Ni, and Zn derivatives. The trace for NiTPP is shown in Figure 1B. From the analysis described above, the Mg, Ni, and Zn compounds appear to be acting as

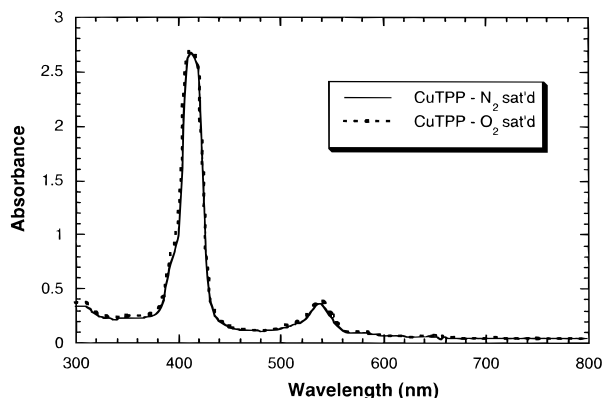


Figure 2. UV-vis spectra of an $\sim 80 \mu\text{M}$ solution of Cu(II)TPP at room temperature in CH_2Cl_2 solution saturated with N_2 (solid line) and O_2 (dashed line). The path length is 1.00 cm.

Lewis acids toward the surface, withdrawing electron density from the bulk semiconductor, if electric field effects are driving the observed PL changes. As noted for the metalloporphyrins that enhanced PL intensity, changing the ligand affects the relative magnitude of the quenching effect: $\text{NiTPP} < \text{MgTPP} \sim \text{ZnTPP}$, but $\text{MgOEP} \sim \text{ZnOEP} < \text{NiOEP}$ when studied on a common CdSe surface. Collectively, our data suggest that there is a subtle interplay of electron density among the metal, ligand, and semiconductor.

Oxygen-Saturated Solution Studies. Given the importance of oxygen-metalloporphyrin interactions, we investigated whether saturation of the methylene chloride solutions with oxygen rather than nitrogen could affect the aforementioned PL responses using identical CdSe substrate surfaces. We estimate that oxygen-saturated solutions of this solvent correspond to a concentration of dissolved oxygen on the order of 10 mM at room temperature.¹⁰

Prior to performing the (metallo)porphyrin adsorption studies, two control experiments were conducted. First, changing the dissolved gas ambient from nitrogen to oxygen had no effect on the CdSe PL intensity. Second, none of the 17 (metallo)porphyrins of this study exhibited any significant change in their electronic absorption spectra (300–800 nm) in CH_2Cl_2 when the dissolved gaseous ambient was changed, supporting the notion that interactions between oxygen and the (metallo)porphyrins are very weak under these conditions. Representative spectral data for CuTPP are shown in Figure 2.

Table 1 summarizes the effect of oxygen on the magnitude and direction of the PL responses. For the porphyrins themselves, we see no evidence that the change in dissolved gas ambient affects the PL response, as PL enhancements and their concentration dependence (vide infra) are about the same within experimental error. In sharp contrast, the PL response of many of the metalloporphyrins is markedly and reversibly perturbed by the introduction of oxygen.

The most dramatic changes are exhibited by the Mg, Ni, and Zn complexes: Instead of quenching PL intensity, as was found in nitrogen-saturated solution, these complexes enhance the PL intensity in oxygen-saturated solution. Typical data for NiTPP are shown in Figure 1C. These three metal complexes give roughly similar responses in the oxygen-containing ambient, with their TPP complexes yielding somewhat larger effects than their OEP complexes. Table 1 demonstrates that some of the other metalloporphyrins examined cause changes in magnitude but not the direction of the PL response, with the ligand again influencing the response. Thus, CoTPP gives a smaller enhancement with oxygen present, but there is no significant change

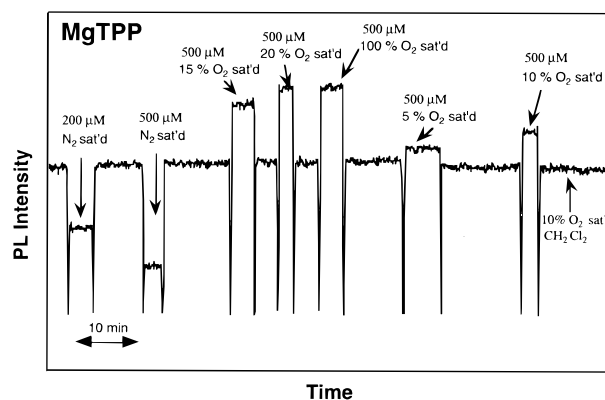


Figure 3. PL intensity from an n-CdSe crystal exposed to a CH_2Cl_2 solution of MgTPP. The CH_2Cl_2 solutions were saturated with N_2 or the indicated percentage of O_2 in an O_2/N_2 mixture as described in the Experimental Section. The concentrations of MgTPP are indicated in the graph. The reference solution before each MgTPP addition is the indicated N_2 or N_2/O_2 -saturated CH_2Cl_2 composition used for that subsequent MgTPP addition.

for CoOEP; CuOEP gives a smaller enhancement with oxygen, but there is little effect of oxygen for CuTPP; and slight increases in response are seen with oxygen for both CdTPP and CdOEP.

An equilibrium for these reactions might be written as



where MP represents a metalloporphyrin and σ represents a surface binding site. We were able to investigate the oxygen dependence of these surface-mediated reactions by varying the oxygen partial pressure. Representative data are shown for MgTPP in Figure 3, which highlight both the readily reversible nature of the oxygen interaction and the fact that saturation of this PL effect occurs by about 20% of the saturated oxygen concentration. We see a similar oxygen concentration dependence for all the metalloporphyrins that exhibited a substantial response to oxygen in solution.

Adsorption Binding Constants. We used the concentration dependence of the PL changes in conjunction with the Langmuir adsorption isotherm model to estimate the equilibrium constant for surface adduct formation in nitrogen- and oxygen-saturated solutions of the (metallo)porphyrins. The model is quantitatively represented by eq 2:¹¹

$$\theta = \frac{KC}{1 + KC} \quad \text{or} \quad \frac{1}{\theta} = \frac{1}{KC} + 1 \quad (2)$$

In the above expression K is the equilibrium constant for adsorption, and C is the molar concentration. The fractional surface coverage, θ , was estimated from the fractional PL changes: When the PL changes have saturated, PL_{sat} , θ is taken to be 1; the PL intensity in the reference ambient, PL_{ref} , corresponds to $\theta = 0$; at intermediate coverages, the PL intensity is designated as PL_x , and defined by eq 3.¹²

$$\theta = \frac{|\text{PL}_x - \text{PL}_{\text{ref}}|}{|\text{PL}_{\text{sat}} - \text{PL}_{\text{ref}}|} \quad (3)$$

A representative plot of θ^{-1} vs C^{-1} is shown in Figure 4 for TPP and demonstrates the good fit typically observed for these systems.

Values for K in both nitrogen- and oxygen-saturated solution for each substrate are summarized in Table 1. For all of the

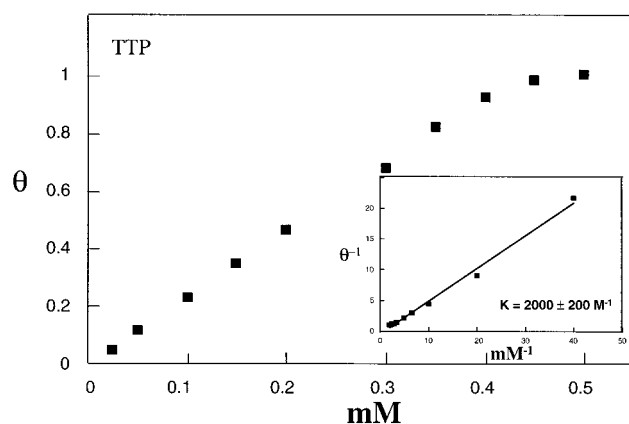


Figure 4. Plot of θ , based on fractional PL changes (eq 3), as a function of concentration for etched CdSe exposed to a N_2 -saturated CH_2Cl_2 solution of tetra-(4-tolyl)porphyrin, TPP. The inset represents the same data as a double-reciprocal plot (eq 2), yielding an equilibrium constant of $2000 \pm 200 M^{-1}$. The PL was excited with 633 nm light and monitored at 720 nm.

compounds examined, the values span a range of only 2 orders of magnitude, from $\sim 10^3$ to $10^5 M^{-1}$. There is very little difference among the porphyrins, whose K values lie at the lower end of this range; and as is seen in their saturation PL enhancements, introduction of oxygen into the porphyrin solutions has little effect on K .

In contrast, the metalloporphyrins exhibit a broader range of binding constants that depend on metal, ligand, and the presence of oxygen. Least affected are the Cd complexes, for which K is constant at $\sim (2-3) \times 10^3 M^{-1}$ across the TPP and OEP complexes and in both gas-saturated ambients. Order-of-magnitude ligand-induced changes in K are seen in nitrogen with Mg and Ni (enhancements in going from the TPP to the OEP complex) and with Co (enhancement in going from the OEP to the TPP complex). Order-of-magnitude oxygen-induced reductions in K are seen with CoTPP, NiOEP, and ZnOEP. The largest values of K , on the order of $10^5 M^{-1}$, were found for NiOEP, ZnTPP, ZnOEP, and CoTPP, all in nitrogen.

Film Studies. Exposure of CdSe to gaseous oxygen causes a negligible PL change relative to the PL intensity in a nitrogen reference ambient. Given the effect of oxygen on adsorption of many of these metalloporphyrins in solution and our previous success using metal complexes as film transducers for gas detection on CdSe,² we investigated oxygen effects on PL from metalloporphyrin-coated CdSe. Films of porphyrins and metalloporphyrins were prepared by simply placing drops of the compounds dissolved in methylene chloride solution onto the CdSe substrate and allowing the solvent to evaporate. If uniform coverage is assumed, the deposited material would correspond to an average thickness of $\sim 0.1 \mu m$.

As expected from solution studies, films of the porphyrins and of CdTPP and CdOEP yielded no PL response to oxygen. However, films of all of the other metalloporphyrins did mediate a PL response to oxygen, as summarized in Table 2. A typical PL trace is shown in Figure 5, which presents oxygen-induced PL quenching observed for a CoTPP-coated sample. The direction of the PL response is consistent with conversion of the film to a more electron-withdrawing structure upon oxygenation, if driven by electric field changes, as noted above. This is the direction of the PL response for all but NiTPP and ZnTPP films, for which exposure to oxygen enhances the PL intensity. Typical percent changes in PL intensity at saturation

TABLE 2: PL Ratios and Binding Constants for Films

compound	PL ratio ^a	K (atm ⁻¹) ^b
Mg(II) TPP	0.81	0.6
Co(II) TPP	0.86	2.9
Ni(II) TPP	1.13	1.2
Cu(II) TPP	0.88	4.2
Zn(II) TPP	1.30	1.1
Mg(II) OEP	0.88	1.3
Co(II) OEP	0.79	4.2
Ni(II) OEP	0.77	1.4
Cu(II) OEP	0.89	8.1
Zn(II) OEP	0.76	2.3

^a The ratio of PL intensity for CdSe coated with a film of the indicated compound (see Experimental Section) upon exposure to O_2 (when PL changes were saturated) relative to the PL intensity in N_2 . The excitation wavelength was 633 nm, and the PL intensity was measured at 720 nm. ^b Equilibrium binding constants determined from fits to the Langmuir adsorption isotherm model, eq 2; see text regarding the interpretation of these values. The error in the Langmuir fit was generally less than 10%.

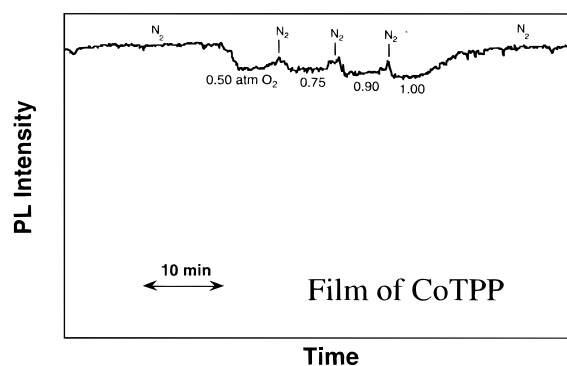


Figure 5. PL intensity changes of an etched n-CdSe crystal coated with a film of CoTPP when exposed to N_2 , O_2 , and N_2/O_2 mixtures, as described in the Experimental Section; the partial pressure of O_2 is indicated in the figure. The total pressure in all cases was 1 atm. The PL was excited with 633 nm light and monitored at 720 nm.

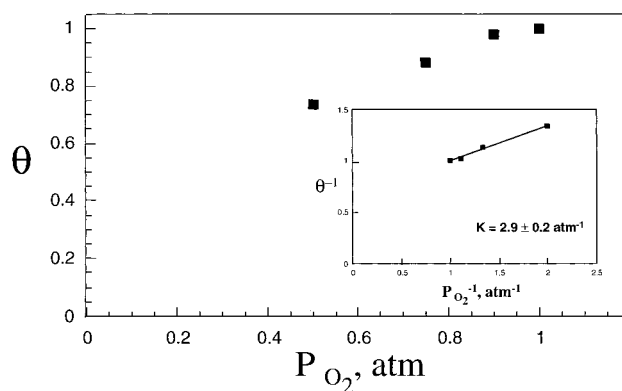


Figure 6. Plot of θ , based on fractional PL changes (eq 3) of the data in Figure 5, vs partial pressure of oxygen. The inset shows the double-reciprocal plot of the same data (eq 2), yielding an equilibrium constant of $2.9 \pm 0.2 atm^{-1}$.

are modest for all films, about 20–25%, but we have not attempted to optimize the deposition procedure to enhance the response.

Use of data like that shown in Figure 5 permits an estimate of film binding constants for oxygen using the Langmuir adsorption isotherm model (eq 2, expressed in terms of pressure), as illustrated in Figure 6. These estimates are for binding at the semiconductor–film interface and may or may not reflect binding in the bulk film.^{2a} Table 2 summarizes the film experiment results. Binding constants range only from ~ 1 to

10 atm⁻¹, and, as typified by the Figures 5 and 6 data, the response requires pressures of several tenths of an atmosphere and saturates near 1 atm.

Binding Factors. In nitrogen-saturated solutions the differences observed in PL signatures among the porphyrins and metalloporphyrins indicate that both steric and electronic effects are important, as there is no obvious trend with such properties as redox potentials,¹³ size, and shape⁹ that can account for the great diversity of responses observed. Moreover, the extensive π system of the porphyrins and d orbitals of the metal ions could permit net transfer of electron density either to or from the semiconductor, with the extent of such charge transfer likely a sensitive function of the adsorbate binding environment.

For many of the metalloporphyrins our observed PL changes lead us to the conclusion that oxygen participates in some kind of adduct with the semiconductor surface and metalloporphyrin. To our knowledge, the only previous study of a system comprising metalloporphyrin, oxygen, and a CdS(e) semiconductor surface is by Chrysochoos and co-workers,^{6,7} who found slight variations in binding constants to nonstoichiometric CdS clusters through comparisons of PL intensity quenching by the same TPP complexes (M = Mg, Zn, Cd, Cu, Ni, Co) in deaerated and air-saturated solutions. These studies, however, were conducted in 2-propanol. In subsequent studies on CdS nanoparticles in contact with CuTPP,¹⁴ the same researchers proposed the formation of S²⁻—Cu²⁺ bonds, leading to the reduction of Cu²⁺ to Cu⁺. We could have a similar kind of Se²⁻—M²⁺ surface ligation, but our reversible PL results in both N₂- and O₂-saturated solvents suggest that net redox chemistry does not occur under our experimental conditions.

A number of reversible oxygen adducts of metalloporphyrins have been characterized at low temperature, and optical spectroscopy has shown that the O₂—metalloporphyrin interaction is weak.^{4,5} Although the structural nature of the oxygen—metalloporphyrin-surface adduct cannot be defined by our experiments, and we see no evidence for an oxygen—metalloporphyrin adduct in solution, the surface of the semiconductor could certainly facilitate oxygen binding: As the metalloporphyrins come into contact with the CdSe surface, which offers Lewis acidic and basic coordination sites, the resulting steric and electronic perturbation could accommodate formation of an adduct with oxygen. One possible structure would have the dioxygen molecule link the metalloporphyrin to a surface Cd²⁺ site.

Suslick et al.⁴ found evidence at low temperature by EPR (but not by optical spectroscopy) for a 1:1 oxygen adduct with an iron porphyrin and proposed different kinds of interactions that could be involved in its formation, including magnetic exchange, interactions with the π system of the porphyrins, and charge-transfer complex formation,¹⁵ wherein the metalloporphyrin is to some extent oxidized and the oxygen reduced. These kinds of interactions could be occurring in our systems as well, with the origin of the PL response varying with adsorbate structure and electronic properties such as the number of unpaired electrons and their orbital occupancy.

For the films that we have examined, these factors may be important along with others related to packing. Several attempts have been made to mimic cooperative dioxygen binding by using solid metalloporphyrins.^{5,16,17} In one approach Basolo has attached Fe(II)TPP to a rigid modified silica gel support to produce an efficient oxygen carrier.⁵ Suslick and co-workers¹⁷ speculated that as molecules oxygenate, the change in molecular dimensions induces strain in the crystallite. At a certain point

this strain is sufficient to induce a conformational change in the solid. Similar effects could be occurring in the films used in our studies.

Summary

Taken in sum, our data demonstrate convincingly that metalloporphyrins adsorb strongly to single-crystal CdSe surfaces and that for many of these complexes some kind of adduct formation with oxygen occurs that is mediated by the semiconductor surface. The interaction can potentially be used to discriminate among some of these metalloporphyrins, as they exhibit various PL signatures based on the combination of metal and ligand. Other related metalloporphyrins are currently being investigated in our laboratories to better understand these unusual surface adducts.

Acknowledgment. We thank Professors Judith Burstyn, Karl Kadish, Clark Landis, and Kenneth Suslick for helpful discussions. We are grateful to the National Science Foundation for support of this research.

References and Notes

- (1) (a) Lorenz, J. K.; Kuech, T. F.; Ellis, A. B. *Langmuir* **1998**, *14*, 1680. (b) Ellis, A. B.; Brainard, R. J.; Kepler, K. D.; Moore, D. E.; Winder, E. J.; Kuech, T. F.; Lisensky, G. C. *J. Chem. Educ.* **1997**, *74*, 680. (c) Brainard, R. J.; Paulson, C. A.; Saulys, D.; Gaines, D. F.; Kuech, T. F.; Ellis, A. B. *J. Phys. Chem. B* **1997**, *101*, 11180. (d) Kepler, K. D.; Lisensky, G. C.; Patel, M.; Sigworth, L. A.; Ellis, A. B. *J. Phys. Chem.* **1995**, *99*, 16011.
- (2) (a) Brainard, R. J.; Ellis, A. B. *J. Phys. Chem. B* **1997**, *101*, 2533. (b) Moore, D. E.; Lisensky, G. C.; Ellis, A. B. *J. Am. Chem. Soc.* **1994**, *116*, 9687.
- (3) (a) Sternberg, E. D.; Dolphin, D.; Bruckner, C. *Tetrahedron* **1998**, *54*, 4151. (b) Shelnutt, J. A.; Song, X. Z.; Ma, J. G.; Jia, S. L.; Jentzen, W.; Medforth, C. J. *Chem. Soc. Rev.* **1998**, *27*, 31. (c) Dolphin, D.; Traylor, T. G.; Xie, L. Y. *Acc. Chem. Res.* **1997**, *30*, 251. (d) Aida, T.; Inoue, S. *Acc. Chem. Res.* **1996**, *29*, 39. (e) Bertini, I.; Gray, H. B.; Lippard, S. J.; Valentine, J. S. *Bioinorganic Chemistry*; University Science Books: Sausalito, CA, 1994; (f) Smith, K. M. *Porphyrins and Metalloporphyrins*; Elsevier Scientific Publishing Company: New York, 1975.
- (4) Bocian, D. F.; Findsen, E. W.; Hofman, J. A.; Schick, G. A.; English, D. R.; Hendrickson, D. N.; Suslick, K. S. *Inorg. Chem.* **1984**, *23*, 800.
- (5) Leal, O.; Anderson, D. L.; Bowman, R. G.; Basolo, F.; Burwell, R. L. *J. Am. Chem. Soc.* **1975**, *97*, 5125.
- (6) Chrysochoos, J. *J. Phys. Chem.* **1992**, *96*, 2868.
- (7) Bhamro; Chrysochoos, J. *J. Lumin.* **1994**, *60–61*, 359.
- (8) Murphy, C. J.; Lisensky, G. C.; Leung, L. K.; Kowach, G. R.; Ellis, A. B. *J. Am. Chem. Soc.* **1990**, *112*, 8344.
- (9) Koerner, R.; Wright, J. L.; Ding, X. D.; Nasset, M. J. M.; Aubrecht, K.; Watson, R. A.; Barber, R. A.; Mink, L. M.; Tipton, A. R.; Norvell, C. J.; Skidmore, K.; Simonis, U.; Walker, F. A. *Inorg. Chem.* **1998**, *37*, 733 and references therein.
- (10) Fogg, P. G. T.; Gerrard, W. *Solubility of Gases in Liquids*; John Wiley & Sons: New York, 1991; pp 277–295.
- (11) Atkins, P. W. *Physical Chemistry*, 6th ed.; W. H. Freeman and Co.: New York, 1998; pp 858–862.
- (12) Winder, E. J.; Kuech, T. F.; Ellis, A. B. *J. Electrochem. Soc.* **1998**, *145*, 2475.
- (13) Values of $E_{1/2}$ for the oxidation and reduction of (metallo)TPP and (metallo)OEP species have been reported in N₂-saturated aprotic solvents and span a relatively narrow range across the series of compounds we have examined. However, the experimental conditions do differ from those we have employed, limiting our ability to make correlations of PL response with (metallo)porphyrin redox properties. See ref 3f and the following. (a) Walker, F. A.; Beroiz, D.; Kadish, K. M. *J. Am. Chem. Soc.* **1976**, *98*, 3484. (b) Kadish, K. M.; Morrison, M. M. *J. Am. Chem. Soc.* **1976**, *98*, 3326.
- (14) (a) Isarov, A. V.; Chrysochoos, J. *Langmuir* **1997**, *13*, 3142. (b) Isarov, A. V.; Chrysochoos, J. *Proc. Indian Acad. Sci., Chem. Sci.* **1998**, *110*, 277.
- (15) Rosenberg, B.; Camiscoli, J. F. *J. Chem. Phys.* **1961**, *35*, 982.
- (16) Jones, R. D.; Summerville, D. A.; Basolo, F. *J. Am. Chem. Soc.* **1978**, *100*, 4416 and references therein.
- (17) Jameson, G. B.; Molinaro, F. S.; Ibers, J. A.; Collman, J. P.; Brauman, J. I.; Rose, E.; Suslick, K. *J. Am. Chem. Soc.* **1980**, *102*, 3224.