Photoluminescent Properties of Cadmium Selenide in Contact with Solutions and Films of Metalloporphyrins: Nitric Oxide Sensing and Evidence for the Aversion of an Analyte to a Buried Semiconductor−Film Interface

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Abstract: The band-edge photoluminescence (PL) intensity of etched n-CdSe single crystals is quenched reversibly by adsorption of the trivalent metalloporphyrins, MTPPCl (TPP = tetraphenylporphyrin; M = Mn, Fe, Co) in nitrogen-saturated methylene chloride solution. The PL responses are concentration dependent and can be fit to the Langmuir adsorption isotherm model to yield binding constants of $\sim 10^3-10^4$ M^{-1}. The MTPPCl compounds react irreversibly with NO in solution to form nitrosyl adducts, and these compounds reversibly enhance the CdSe PL intensity when adsorbed onto the semiconductor surface, also with binding constants of $\sim 10^3-10^4$ M^{-1}. Films of MTPPCl were prepared on CdSe substrates by solvent evaporation. These coatings serve as transducers for NO detection: while the bare CdSe surface shows no response to NO gas relative to N_2, the coated surfaces reversibly enhance the PL intensity (CoTPPCl) or quench it (MnTPPCl and FeTPPCl), with binding constants on the order of ~ 1 atm^{-1}. In contrast to the PL results, which are particularly sensitive to the semiconductor−film interface, electronic and IR spectral changes of the bulk film induced by NO binding were irreversible. The UV−vis and IR spectra could be spectroscopically mimicked by preformed nitrosyl adduct films that were prepared by solvent evaporation of MTPPCl (M = Co, Fe) and MTPP (M = Co) solutions that had been exposed to NO. These films, however, lack transduction capability, as the PL intensity is the same in NO and N_2 ambients. For the films prepared from FeTPPCl and CoTPPCl, the saturation of IR and UV−vis spectral changes occurs at NO pressures at least 10-fold lower than observed for PL changes. These results indicate that NO has a strong aversion to binding at the semiconductor−film interface as opposed to the bulk film environment. Steric and electronic contributions to these observed effects are discussed.

Introduction

Recent research developments have highlighted the critical role that nitric oxide, NO, plays in a variety of physiological processes.[1−3] For example, NO has been found to serve as a biological messenger in neurotransmission and to assist the immune system in destroying tumor cells and intracellular parasites. The importance of NO has prompted efforts to develop sensors that can detect this species under a variety of experimental conditions.[4−8] Methods used to date have largely been based on changes in electronic absorption spectra and electrochemical properties. For example, Malinski and co-workers have developed an amperometric sensor based on a porphyrin-catalyzed oxidation reaction.[6] Sailor et al. have reported reversible photoluminescence (PL) changes on binding of NO to porous silicon.[4]

Because NO is known to react with a variety of metalloporphyrins, often causing substantial changes in metal coordination environment and electronic structure, these compounds potentially serve as a rich source of sensor transduction strategies.[9−11] We and others have used the photoluminescence (PL) of semiconductor substrates such as CdS and CdSe to demonstrate that divalent metalloporphyrins (MPs) bind strongly to the surfaces of these substrates, and that adsorption can be substantially influenced by the presence of ligands such as oxygen that bind to the MPs.[12−16] Many adsorbates have the ability to act as Lewis acids or bases toward the solid, shifting electron density into or out of surface electronic states and thereby expanding or contracting the depletion width of the semiconductor, respectively. If a region on the order of the depletion width is regarded as nonemissive (a "dead layer") insofar as PL is concerned, the electric field therein separates

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[1] Traylor, T. G.; Sharma, V. S. *Biochemistry* **1992**, *31*, 2847.
[2] Butler, A. R.; Williams, D. L. H. *Chem. Rev. Soc.* **1993**, *22*, 233.
[3] Feldman, P. L.; Griffith, O. W.; Stuehr, D. J. *Chem. Eng. News* **1993**, Dec 20, 26.
[4] Harper, J.; Sailor, M. J. *Anal. Chem.* **1996**, *68*, 3713.
[5] Zhou, X.; Arnold, M. A. *Anal. Chem.* **1996**, *68*, 1748.
[6] Malinski, T.; Taha, Z. *Nature* **1992**, *358*, 676.
[7] Tschudi, M. R.; Mesaros, S.; Luscher, T. F.; Malinski, T. *Hypertension* **1996**, *27*, 32.
[8] Bennett, J. E.; Malinski, T. *Chem. Mater.* **1991**, *3*, 490.
[9] Scheidt, W. R. *Acc. Chem. Res.* **1977**, *10*, 339.
[10] Scheidt, W. R.; Ellison, M. K. *Acc. Chem. Res.* **1999**, *32*, 350.
[11] Hoshino, M.; Laverman, L.; Ford, P. C. *Coord. Chem. Rev.* **1999**, *187*, 75.
[12] Ivanisevic, A.; Ellis, A. B. *J. Phys. Chem. B* **1999**, *103*, 1914.
[13] Chrysochoos, J. *J. Phys. Chem.* **1992**, *96*, 2868.
[14] Bhamro; Chrysochoos, J. *J. Lumin.* **1994**, *60−61*, 359.
[15] Isarov, A. V.; Chrysochoos, J. *Langmuir* **1997**, *13*, 3142.
[16] Isarov, A. V.; Chrysochoos, J. *Proc. Indian Acad. Sci., Chem. Sci.* **1998**, *110*, 277.

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photogenerated electron−hole pairs rather than permits their recombination. The PL response defines a “luminescent litmus test”, with Lewis acids quenching and Lewis bases enhancing the semiconductor’s PL intensity.[17−22]

Porphyrins and metalloporphyrins are known to organize themselves into crystalline, supramolecular arrays, and the geometry of such arrays has been shown to be highly dependent upon the solvent and local chemical environment.[23−33] Our recent studies demonstrated that the interaction of many divalent metalloporphyrins with single-crystal CdSe surfaces is affected by oxygen, both in solution and in the gas phase.[12] In the latter case, we showed that films of divalent metalloporphyrins deposited onto single-crystal CdSe substrates can serve as transducers toward oxygen, coupling ligation chemistry with changes in the PL of the underlying semiconductor. Because these changes are readily reversible, such structures have the potential to serve as on-line detectors for this analyte.

An important issue associated with such film-coated semiconductor structures is the nature of the buried semiconductor−film interface. Our data for several coated semiconductor structures suggest that partitioning of an analyte A between the bulk film and the buried interface can be detected.[21,34,35] The relevant equilibria are given in eqs 1−3, where, for the present study, **1** is the MP and A (g) is NO. Equation 1 describes the

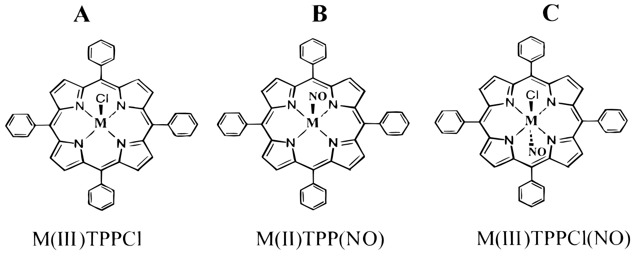
$$\mathrm{A(g)} + \mathbf{1}\mathrm{(f)} \Leftrightarrow \mathbf{1}\cdot\mathrm{A(f)} \qquad (1)$$

$$\mathbf{1}\cdot\mathrm{A(f)} + \mathbf{1}\cdot\sigma \Leftrightarrow \mathbf{1}\cdot\mathrm{A}\cdot\sigma + \mathbf{1}\mathrm{(f)} \qquad (2)$$

$$\mathrm{A(g)} + \mathbf{1}\cdot\sigma \Leftrightarrow \mathbf{1}\cdot\mathrm{A}\cdot\sigma \qquad (3)$$

equilibrium associated with binding of the analyte in the bulk film, **1**(f), to produce **1**·A(f), for which the equilibrium constant K_{film} can be estimated, for example, through electronic absorption or IR spectral changes occurring in the bulk film. In contrast, eq 3 represents binding of the analyte to a molecule of **1** that is localized at a semiconductor surface site $\mathbf{1}\cdot\sigma$, i.e., at the generally different environment of the buried interface, to yield $\mathbf{1}\cdot\mathrm{A}\cdot\sigma$. Our evidence to date indicates that analyte-induced semiconductor PL changes are sensitive specifically to the film monolayer(s) nearest the semiconductor surface and that the equilibrium constant $K_{\mathrm{interface}}$ derived from PL changes is associated with binding at the buried interface. The ratio of $K_{\mathrm{interface}}/K_{\mathrm{film}}$ thus yields the equilibrium constant for eq 2, which is the distribution coefficient that expresses the relative preference of the analyte for the two environments.

Chart 1



We report in this study the successful implementation of a NO detection strategy using metalloporphyrin-mediated effects on the PL of CdSe substrates. These interactions provide a means to characterize a variety of semiconductor−metalloporphyrin interfaces. Specifically, we show that the CdSe PL intensity is reversibly quenched by the adsorption of MTPPCl (M = Mn, Fe, Co) compounds (Chart 1A) in nitrogen-saturated CH_2Cl_2 solution. When the solvent is instead saturated with NO, the nitrosyl adduct of each MP is irreversibly formed in solution (Chart 1B). When these nitrosyl adducts are brought into contact with the semiconductor surface, they cause reversible enhancements in the CdSe PL intensity. Deposition of films of MTPPCl onto CdSe results in coatings that respond reversibly to NO in the solid state, permitting their use as transducers for on-line detection of this analyte. Furthermore, comparisons of binding affinities estimated from PL and from electronic and IR spectroscopic measurements reveal that NO has a strong aversion to the buried semiconductor−film interface, characterized by a partition coefficient on the order of 10^{-1} or less. Steric and electronic effects that might account for this remarkable binding preference are discussed.

Experimental Section

Materials and Sample Preparation. Samples of $\mathrm{Mn^{III}TPPCl}$, $\mathrm{Fe^{III}TPPCl}$, $\mathrm{Co^{III}TPPCl}$, and $\mathrm{Co^{II}TPP}$ were purchased from Porphyrin Products, Logan, UT, and used without further purification. Nitric oxide gas was obtained from Aldrich (98.9%) and purified through a KOH column immediately before each experiment to remove higher nitrogen oxides.[36] Chlorine gas (Cl_2) was purchased from Aldrich (99.5%) and used as received. Methylene chloride (Aldrich, 99+%) was distilled from calcium hydride under nitrogen. ^{15}NO was generated in situ from the reaction of ascorbic acid (Aldrich, 99%) with sodium nitrite (^{15}N, 98+%, Cambridge Isotope Laboratories, Inc, Andover, MA) in an anaerobic aqueous medium. Single-crystal, vapor-grown *c*-plates of n-CdSe, having a resistivity of ∼2 Ω·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. Prior to film deposition the CdSe sample was given a second etch in a solution of concentrated HCl, rinsed with methanol, and then dried in flowing nitrogen.

The nitrosyl adduct of each metalloporphyrin was prepared by bubbling an excess of NO through a methylene chloride solution of each MTPPCl compound, while maintaining rigorously anaerobic conditions. The excess NO was removed by subsequently bubbling dry nitrogen through the solution after nitrosyl formation.

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(17) Murphy, C. J.; Lisensky, G. C.; Leung, L. K.; Kowach, G. R.; Ellis, A. B. *J. Am. Chem. Soc.* **1990**, *112*, 8344.

(18) Lorenz, J. K.; Kuech, T. F.; Ellis, A. B. *Langmuir* **1998**, *74*, 680.

(19) 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.

(20) Brainard, R. J.; Paulson, C. A.; Saulys, D.; Gaines, D. F.; Kuech, T. F.; Ellis, A. B. *J. Phys. Chem. B* **1997**, *101*, 11180.

(21) Brainard, R. J.; Ellis, A. B. *J. Phys. Chem. B* **1997**, *101*, 2533.

(22) Kepler, K. D.; Lisensky, G. C.; Patel, M.; Sigworth, L. A.; Ellis, A. B. *J. Phys. Chem.* **1995**, *99*, 16011.

(23) Sharma, C. V. K.; Broker, G. A.; Huddleston, J. G.; Baldwin, J. W.; Metzger, R. M.; Rogers, R. D. *J. Am. Chem. Soc.* **1999**, *121*, 1137.

(24) Bhyrappa, P.; Wilson, S. R.; Suslick, K. *J. Am. Chem. Soc.* **1997**, *119*, 8492.

(25) Burrell, A. K.; Officer, D. L.; Reid, D. C. W.; Wild, K. Y. *Angew. Chem., Int. Ed.* **1998**, *37*, 114.

(26) Abrahams, B. F.; Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1991**, *113*, 3606.

(27) Abrahams, B. F.; Hoskins, B. F.; Michall, D. M.; Robson, R. *Nature* **1994**, *369*, 727.

(28) Drain, C. M.; Nifiatis, F.; Vasenko, A.; Batteas, J. D. *Angew. Chem., Int. Ed.* **1998**, *37*, 2344.

(29) Linke, M.; Chambron, J.; Heitz, V.; Sauvage, J. *J. Am. Chem. Soc.* **1997**, *119*, 11329.

(30) Turner, P.; Gunter, M. J.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1998**, *51*, 853.

(31) Jentzen, W.; Unger, E.; Song, X. Z.; Jia, S. L.; Tyrk, I. T.; Stenner, R. S.; Dreybrodt, W.; Scheidt, W. R.; Shenutt, J. A. *J. Phys. Chem. A* **1997**, *101*, 5789.

(32) Kumar, R. K.; Balasubramanian, S.; Goldberg, I. *Inorg. Chem.* **1998**, *37*, 541.

(33) Lin, V. S. Y.; DiMagno, S. G.; Therien, M. J. *Science* **1994**, *264*, 1105.

(34) Meeker, K.; Ellis, A. B. *J. Phys. Chem.* **1999**, *103*, 995.

(35) Moore, D. E.; Lisensky, G. C.; Ellis, A. B. *J. Am. Chem. Soc.* **1994**, *116*, 9687.

(36) Richter-Addo, G. B.; Hodge, S. J.; Yi, G.; Khan, M. A.; Ma, T.; Van Caemelbecke, E.; Guo, N.; Kadish, K. M. *Inorg. Chem.* **1996**, *35*, 6530.

Nitrosyl chloride (NOCl) was prepared in situ in a solution of CH_2Cl_2.[37] Initially CH_2Cl_2 was saturated with NO, by bubbling the gas through the solution for 3 min. The presence of NO in the solution was confirmed by its characteristic IR band, ν_{NO}, at 1846 cm^{-1}. Subsequently Cl_2 was bubbled through the solution, and the solution turned dark orange, as previously reported.[37] The observed shift in ν_{NO} to 1852 cm^{-1} confirmed the formation of NOCl in solution.

Apparatus. The sample of CdSe was mounted on a glass rod between two Teflon rings within a glass cell.[17] In the solution experiment a gas flow apparatus was assembled that allowed dry nitrogen to flow through the glass cell where the solid semiconductor crystal was illuminated.[17] A flow meter was used to adjust the flow rate, which varied from 80 to 120 mL/min, and the total gas pressure over the sample was 1 atm.[21] In the film experiments the glass cell was directly connected to the same setup, and two flow meters were used to measure the independently variable concentrations of N_2 and NO, as described previously.[21,34]

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. A cutoff filter was used in the spectrophotometer to permit collection of the band-edge PL at $\lambda_{max} = 720$ nm ($E_g = 1.7$ eV). The entire PL spectrum was monitored, while the PL intensity was tracked 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 analyzed by Oriel Instaspec software for Windows.

Film Preparation. Two methods were used to prepare the MP films and their nitrosyl adducts. In the *direct method*, the MPs were dissolved in methylene chloride solution (~400 μM). Prior to the PL experiments two drops of the solutions were deposited on n-CdSe crystals and dried under a stream of N_2, forming films with an estimated thickness of 0.1 μm if uniform deposition is assumed. PL experiments were also conducted with *preformed* films of the nitrosyl adducts of the MPs. The MP nitrosyls were preformed in solution by bubbling NO through the solution for at least 3 min. The nitrosyl adduct was then deposited in the same fashion as the parent MP on the single crystal. Both methods were used to prepare films for electronic spectroscopy experiments. In these cases the films were evaporated under strictly anaerobic conditions on the sides of a quartz cuvette.

IR Studies. Surface IR measurements of films of the MPs and their nitrosyl adducts were conducted using the synchrotron source at the University of Wisconsin Synchrotron Radiation Center. Samples of the CdSe crystals were polished with 0.3 μm alumina prior to the deposition of the film in order to slightly roughen the surface. The rough surface produced better IR data than the etched semiconductor surface; the latter resulted in oriented deposition of the metalloporphyrin parallel to the surface and led to a double pass interference effect. To obtain good quality spectra each polished crystal (ca. 1.0 × 1.0 × 0.1 cm) was partially coated with a solution of the appropriate MP (~400 μM) in methylene chloride, followed by slow evaporation of the solvent in a closed container under a stream of nitrogen. The samples were analyzed in transmission mode using a NicPlan microscope enclosed in a dry nitrogen purged chamber. The microscope was interfaced to a Nicolet Magna 55011 IR spectrometer, equipped with a liquid nitrogen cooled 1/4 mm MCT detector. The mapping stage installed on the microscope was used to survey the sample surface and showed that the film thickness was highly nonuniform. The part of the CdSe surface that was *not* coated with the film was used to collect the reference spectrum, and patches of film areas were used to collect the sample IR spectra. The spectra were collected using 200 scans and 1 cm^{-1} resolution at a magnification of 32×. The mirror velocity was set at 0.6329 cm/s in order to avoid interference from the 60 Hz component of the synchrotron beam and provide an acceptable signal-to-noise ratio in the spectra.

Electronic Spectroscopic Measurements. The solution UV−vis spectrum of each sample was obtained on a Hewlett-Packard HP89530A spectrophotometer at room temperature between 200 and 800 nm. All compounds in this study exhibited negligible absorbance at the 633 nm excitation and 720 nm CdSe emission wavelengths, and the solution spectra matched those previously reported.[36,38−40] Solid-state UV−vis spectroscopy was used to monitor the binding of NO to the CoTPPCl and FeTPPCl complexes when deposited as films.

EPR Measurements. The X-band (9.2 GHz) EPR spectrum of the NO adduct of Fe^{III}TPPCl in methylene chloride was recorded at 77 K. The spectrum was recorded on a Bruker ESP 300E X-band spectrometer equipped with an EIP model 625 A CW microwave counter. A triplet signal was observed, characteristic of five-coordinate FeTPP(NO).[41−43]

Proton NMR Measurements. The ^1H NMR spectra of the NO adducts of Co^{III}TPPCl and Mn^{III}TPPCl in N_2-saturated $CDCl_3$ were recorded with a Bruker AC-300 spectrometer. The chemical shifts obtained were in good agreement with literature values for the known MTPPNO complexes.[36,38−40]

Results and Discussion

Samples of CdSe exhibit red band-edge PL ($E_g = 1.7$ eV; $\lambda_{max} \sim 720$ nm) when excited with ultra-band-gap excitation. Because the metalloporphyrins of Chart 1 employed in this study are highly colored, excitation was restricted to 633 nm, where there is negligible absorption by the MTPPCl (M = Mn, Fe, Co) compounds. The CdSe samples show negligible PL intensity changes referenced to N_2 when exposed to NO, either in the gas phase or in CH_2Cl_2 solution. However, in the presence of a film or CH_2Cl_2 solution of MTPPCl compounds, addition of NO causes substantial changes in PL properties. Sections below describe the reactions of NO with solutions and films of MTPPCl compounds, using PL changes to estimate adsorption binding constants to the CdSe surface, and electronic spectral changes to estimate film binding affinity for NO. In the final section, we examine aspects of the coordination chemistry of the MTPPCl compounds that could contribute to the spectroscopic effects observed.

I. Nitrogen-Saturated Solution Studies. When each of the MTPPCl compounds is added to a nitrogen-saturated CH_2Cl_2 solution, quenching of the CdSe PL intensity is observed. Figure 1A presents typical data for titration with MnTPPCl. Quenching typically onsets at a concentration of 20−50 μM, and the effect saturates in the range 350−500 μM. The effect is readily reversible, with a solvent rinse serving to restore the original PL intensity, as illustrated in Figure 1A. PL quenching is consistent with the analyte acting as a Lewis acid toward the surface, possibly through withdrawal of electron density from the semiconductor into the porphyrin's aromatic system.[19] Table 1 reveals that all three MTPPCl compounds elicit similar PL responses, although our data do not allow us to know whether the same kind and number of sites are used for binding in each case. In our previous study with divalent metalloporphyrins, we found that the PL response depended on the identity of both the metal and the porphyrin.[12]

The concentration dependence of the PL changes observed permits a rough estimate of the adsorption binding constant through use of the Langmuir adsorption isotherm model.[44] The model is quantitatively represented by eq 4,

$$\theta = KC/(1 + KC) \qquad \text{or} \qquad 1/\theta = (1/KC) + 1 \tag{4}$$

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[37] Vorobyova, O. I.; Dunaeva, K. M.; Ipolitova, E. A.; Tamm, N. S. *Practical Inorganic Chemistry*; Mir Publishers: Moscow, 1987.

[38] Hoshimo, M.; Kogure, M. *J. Phys. Chem. B* **1989**, *93*, 5478.

[39] Scheidt, W. R.; Frisse, M. E. *J. Am. Chem. Soc.* **1975**, *97*, 17.

[40] Scheidt, W. R.; Hatano, K.; Rupprecht, G. A.; Piciulo, P. L. *Inorg. Chem.* **1979**, *18*, 292.

[41] Stone, J. R.; Sands, R. H.; Dunham, R.; Marletta, M. A. *Biochem. Biophys. Res. Commun.* **1995**, *207*, 572.

[42] Wayland, B. B.; Olson, L. W. *J. Am. Chem. Soc.* **1974**, *96*, 6037.

[43] Bohle, D. S.; Hung, G. H. *J. Am. Chem. Soc.* **1995**, *117*, 9584.

[44] Atkins, P. W. *Physical Chemistry*; W. H. Freeman and Co: New York, 1998.

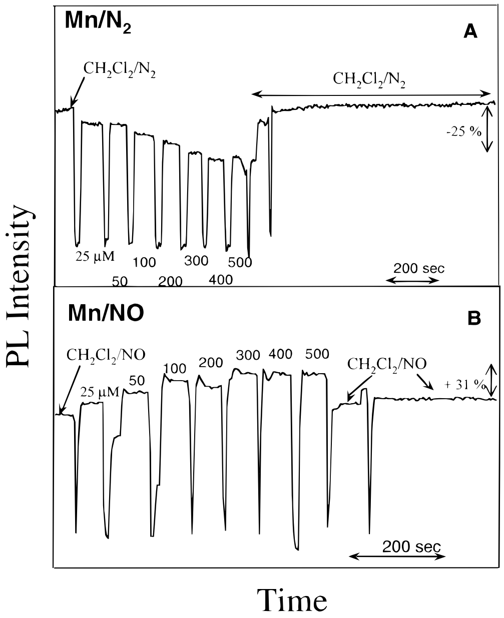

Figure 1. Changes in the PL intensity of an etched n-CdSe sample resulting from exposure to (A) MnTPPCl dissolved in N$_2$-saturated CH$_2$Cl$_2$ and (B) MnTPPCl dissolved in NO-saturated CH$_2$Cl$_2$, forming the nitrosyl adduct. The PL was excited in each case with 633 nm light and monitored at 720 nm. The downward spikes result from draining the sample cell when changing solutions. The bottom of the plots in A and B corresponds to zero PL intensity.

Table 1. PL Results in Solution[a]

compound	PL ratios[b]	K (M^{-1})[c]	PL ratios[d]	K (M^{-1})[e]
Mn^{III}TPPCl	0.75	8 × 10^3	1.31	14 × 10^3
Fe^{III}TPPCl	0.29	33 × 10^3	1.40	30 × 10^3
Co^{III}TPPCl	0.55	12 × 10^3	1.95	8 × 10^3

[a] PL ratios and binding constants based on adsorption of the indicated M^{III}TPPCl compounds onto CdSe in N$_2$- and NO-saturated CH$_2$Cl$_2$ solutions. All data were obtained using the same CdSe sample. [b] The ratio of CdSe PL intensity upon addition of the indicated compound to N$_2$-saturated CH$_2$Cl$_2$ solution (when PL changes were saturated with adsorbate concentration) relative to the PL intensity in N$_2$-saturated CH$_2$Cl$_2$ solvent. The excitation wavelength was 633 nm, and PL intensity was measured at 720 nm. The error in a single measurement was less than 5%. [c] Equilibrium binding constants for adsorption of the indicated compound in nitrogen-saturated CH$_2$Cl$_2$ solution onto CdSe, obtained from fits to the Langmuir adsorption isotherm model, eq 4. The error in the Langmuir fit was generally less than 10%. [d] PL ratio as defined in footnote *b*, except that all data were obtained with NO-saturated CH$_2$Cl$_2$ solutions, leading to the formation of nitrosyl metalloporphyrin adducts in the sample cell. [e] Equilibrium binding constants as described in footnote *c*, except that all data were obtained with NO-saturated CH$_2$Cl$_2$, leading to the formation of nitrosyl metalloporphyrin adducts in the sample cell.

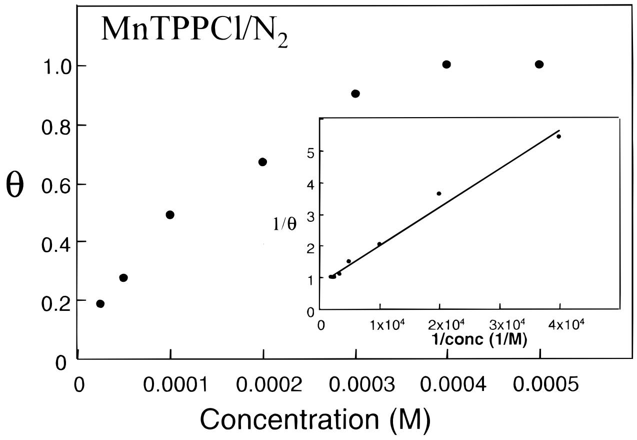

Figure 2. Plot of θ, based on fractional PL changes of the data in Figure 1A (eq 5), as a function of concentration for an etched CdSe sample exposed to a N$_2$-saturated CH$_2$Cl$_2$ solution of MnTPPCl. The inset presents the same data as a double-reciprocal plot, yielding an equilibrium constant of (8.0 ± 0.4) × 10^3 M^{-1}. The PL was excited with 633 nm light and monitored at 720 nm.

where K is the equilibrium constant for adsorption and C is the molar concentration. The fractional surface coverage, θ, is 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 covarages, the PL intensity is designated as PL$_x$ and defined by eq 5.[45]

$$\theta = |(\mathrm{PL}_x - \mathrm{PL}_{\mathrm{ref}})|/|(\mathrm{PL}_{\mathrm{sat}} - \mathrm{PL}_{\mathrm{ref}})| \qquad (5)$$

A representative plot of θ^{-1} vs C^{-1} is shown in Figure 2 for MnTPPCl and demonstrates a reasonably good fit, leading to a value for K of 8 × 10^3 M^{-1}. Table 1 shows that all three MTPPCl compounds yield similar binding constants of 10^3−10^4 M^{-1}, suggesting that variation in the metal exerts only a modest influence on binding affinity.

II. Nitric Oxide Saturated Solution Studies. A control experiment for our studies is the effect on CdSe PL intensity of saturating the CH$_2$Cl$_2$ solvent with NO. We estimate that the concentration of NO in this solvent at atmospheric pressure is in the range ∼1−10 mM.[46] We find no effect on the semiconductor's PL intensity on switching between N$_2$- and NO-saturated solvent.

It is well-known that NO reacts irreversibly with some MTPPCl compounds in solution.[36,38−40] The first equivalent of NO reduces the metalloporphyin to M^{II}TPP and forms NOCl.[42,47,48] The excess NO bubbled through the solution results in the formation of the nitrosyl adduct (Chart 1B). In principle, NOCl, too, could affect the semiconductor's PL intensity. We prepared a solution of NOCl in situ in CH$_2$Cl$_2$ by reacting NO with Cl$_2$.[37] Although a dark orange solution was produced, characteristic of NOCl, we saw no effect on the CdSe PL intensity in this medium relative to the PL intensity in N$_2$- or NO-saturated CH$_2$Cl$_2$.

We have confirmed that the reaction of MTPPCl with NO yields the nitrosyl adducts in CH$_2$Cl$_2$ solution by a variety of spectroscopic techniques. Exposure to NO causes significant and irreversible color changes, and the corresponding spectral changes for all three metal complexes match literature reports.[9,39,40] Agreement with the literature was also found by EPR measurements of the Fe complex and by ^{1}H NMR measurements of the Mn and Co complexes.[36,38−43]

When MTPPCl complexes were dissolved in CH$_2$Cl$_2$ solutions and NO was used to saturate the mixture, completely different PL behavior is observed relative to the N$_2$-saturated CH$_2$Cl$_2$ solution experiments discussed above. As depicted in Figure 1B, an enhancement of PL intensity is seen when the nitrosyl adduct of the Mn complex is present. Table 1 indicates that similar results are found for all three metal complexes investigated. The PL response saturated above a ratio of ∼20% NO in N$_2$.

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(45) Winder, E. J.; Kuech, T. F.; Ellis, A. B. *J. Electrochem. Soc.* **1998**, *145*, 2475.

(46) Fogg, P. G. T.; Gerrard, W. *Solubility of Gases in Liquids*; John Wiley & Sons: New York, 1991.

(47) Scheidt, W. R.; Hoard, J. L. *J. Am. Chem. Soc.* **1973**, *95*, 8281.

(48) Wayland, B. B.; Olson, L. W. *Inorg. Chim. Acta* **1974**, *11*, L23.

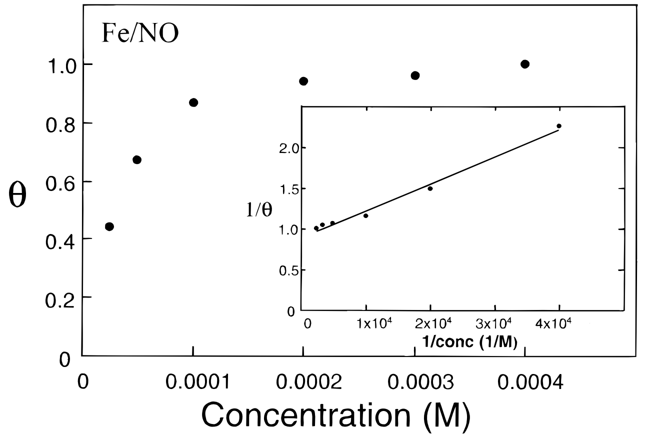

Figure 3. Plot of θ, based on fractional PL changes, as a function of concentration for an etched CdSe sample exposed to a NO-saturated CH_2Cl_2 solution of FeTPPCl. The inset represents the same data as a double-reciprocal plot, yielding an equilibrium constant of $(3.0 \pm 0.1) \times 10^4\ M^{-1}$. The PL was excited with 633 nm light and monitored at 720 nm.

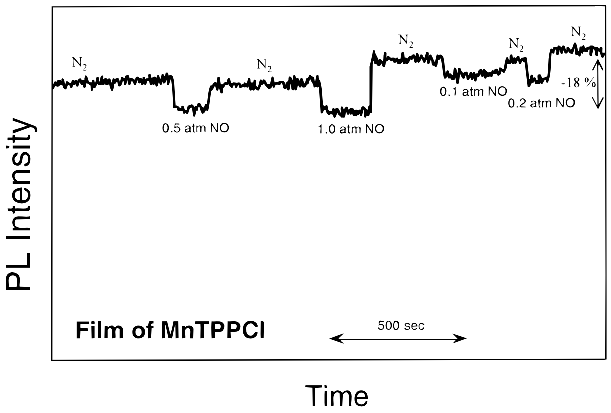

Figure 4. PL intensity changes of an etched n-CdSe crystal coated with a film of MnTPPCl and then exposed to N_2, NO, and N_2/NO mixtures, as described in the Experimental Section; the partial pressure of NO is indicated in the figure. The total pressure in all cases was 1.0 atm. The PL was excited with 633 nm light and monitored at 720 nm. The bottom of the plot corresponds to zero PL intensity.

As an independent test of the species causing the PL change, we investigated the divalent precursor, CoTPP. When this species was dissolved in CH_2Cl_2 and NO was bubbled through the solution, the same product resulted, CoTPP(NO), as was formed using CoTPPCl as a starting material, based on UV−vis spectra.[36,38−40] Likewise, we recorded identical PL enhancements due to exposure of the crystal to a solution of CoTPP(NO) prepared from the two different Co porphyrins. These data confirm that the Co porphyrin nitrosyl species is responsible for the observed PL response.

The direction of the PL change for the nitrosyl adduct adsorbates is consistent with donation of electron density from the adsorbate to the semiconductor, assuming electric field effects are driving the PL changes. Whether the differences shown in Table 1 for the three metal complexes are due to differences in intrinsic basicity or to number and types of binding sites cannot be addressed by our data. Table 1 also includes binding constants for the nitrosyl solution adduct of each metalloporphyrin with the CdSe surface based on PL response, and a typical Langmuir plot is shown in Figure 3. These values are almost the same as those for the corresponding MTPPCl complexes, within experimental error, suggesting that formation of a nitrosyl adduct has little effect on binding affinity to the semiconductor surface.

One additional solution experiment that was conducted involved trying to reverse the effects of FeTPP(NO) adsorption on CdSe PL intensity by returning to a N_2-saturated solution. Once NO has been introduced, subsequent introduction of N_2 with displacement of NO from the CH_2Cl_2 solution causes no change in the CdSe PL intensity. This observation is consistent with the strong affinity of NO for the metal center; N_2 does not displace NO from the metalloporphyrin. If the metal complex is completely removed from the system, however, by repeated solvent rinses, the original PL intensity in the N_2-saturated solvent can be recovered. The solution formation of a nitrosyl adduct with the other two porphyrins, CoTPPCl and MnTPPCl, was "tracked" by PL in a similar fashion with analogous results.

III. Film Studies. PL Results. When gaseous NO is allowed to come into contact with the surface of etched CdSe, the PL intensity of the semiconductor remains constant within experimental error of its intensity in a N_2 ambient. To test the ability of MTPPCl films to serve as transducers for NO detection, a film of each MTPPCl compound was prepared on a CdSe substrate by placing a few drops of a CH_2Cl_2 solution on the surface and allowing the solvent to evaporate in an anaerobic ambient. If uniform coverage is assumed, the deposited material would correspond to an average film thickness of approximately 0.1 μm.

Films of all three metalloporphyrins were found to mediate a PL response to NO. A representative PL trace is presented in Figure 4, which shows NO-induced PL quenching obtained with a Mn^{III}TPPCl-coated substrate. The quenching of the PL intensity in response to NO is indicative of the conversion of the film to a more electron-withdrawing structure upon addition of NO. Quenching of the PL intensity was observed for both the Mn and Fe derivatives; however, the Co complex showed the opposite effect, an enhancement, indicating that the introduction of NO causes donation of electron density to the semiconductor relative to the unreacted film. Most of the changes observed were modest, typically less than ~20% between ~0.1 and 1.0 atm, but no attempt was made to optimize the deposition procedure to enhance the response. In contrast, another NO sensor based on porous silicon was reported to yield larger PL responses that onset at ppm concentration levels.[4] Also noteworthy from Figure 4 is the fact that the NO-induced PL changes are readily reversible once the ambient is restored to pure N_2, although some baseline drift occurs over the course of the experiment.

The type of data gathered in Figure 4 permits an estimate of film binding constants for NO with the three metalloporphyrin films using the Langmuir adsorption isotherm model (eq 4, expressed in terms of pressure). A typical result is shown in Figure 5. Table 2 summarizes the film experiments and reveals that binding constants for all of these samples are on the order of ~1 atm^{-1}. As noted in the Introduction, we believe that these values are rough measures of the affinity of NO to bind to the buried MTPPCl−CdSe interface, $K_{\text{interface}}$.

We explored the question of whether deposition of a nitrosyl adduct directly from CH_2Cl_2 solution could be used to prepare the transducer film instead of deposition of the trivalent MTPPCl film. We investigated this possibility by preparing nitrosyl adducts by bubbling NO through a CH_2Cl_2 solution of FeTPPCl or CoTPPCl and allowing drops of this solution placed on a CdSe surface to evaporate in a container under a stream of N_2. In contrast to the properties of the MTPPCl films, neither of these films could be used as a transducer: switching between NO and N_2 ambients caused no PL change in the CdSe substrate.

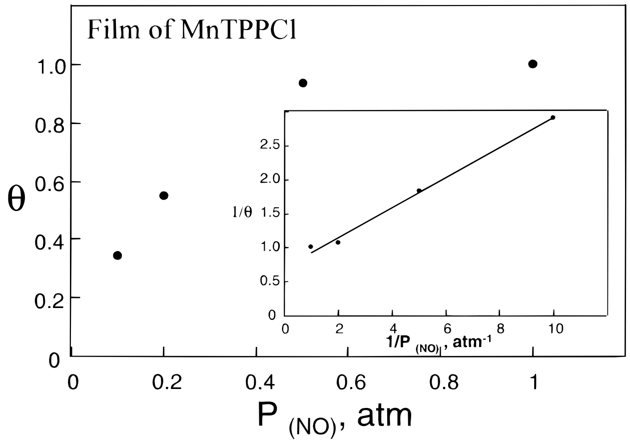

Figure 5. Plot of θ, based on fractional PL changes (eq 5) of the data in Figure 4, vs partial pressure of nitric oxide. The inset shows the double-reciprocal plot of the same data, yielding an equilibrium constant of 4.5 ± 0.4 atm^{-1}.

Table 2. PL Results for Films

compound	PL ratios[a]	K (atm^{-1})[b]
$Mn^{III}TPPCl$	0.82	4.5
$Fe^{III}TPPCl$	0.77	1.0
$Co^{III}TPPCl$	1.36	0.8

[a] The ratio of PL intensity for CdSe coated with a film of the indicated compound (see Experimental Section) upon exposure to NO (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 4. The error in the Langmuir fit was generally less than 10%.

The IR spectra of films of MTPP(NO), deposited from solutions of NO-exposed MTPPCl (M = Fe or Co), also remained unchanged after repeated exposure to excess NO or N_2 gas. The Mn case was not examined due to the extreme air sensitivity of the nitrosyl film.

IR and Electronic Spectroscopy Results. Our PL studies of films prompted us to examine other techniques to further characterize the binding of NO to a solid metalloporphyrin film deposited on a semiconductor substrate. In the previous section we described two distinct methods that resulted in the formation of a nitrosyl adduct on the CdSe surface, summarized by eqs 6 and 7. Equation 6 describes the equilibrium associated with

$$\mathrm{MP(f)} + \mathrm{NO(g)} \leftrightarrow \mathrm{MP(NO)(f)_{direct}} \qquad (6)$$

$$\mathrm{MP(solv)} + \mathrm{NO(g)} \Rightarrow \mathrm{MP(NO)(solv)} \Rightarrow \mathrm{MP(NO)(f)_{preformed}} \qquad (7)$$

binding NO gas to a bulk film of a metalloporphyrin (MP) coated onto the semiconductor surface, to produce MP(NO)-$(f)_{direct}$, which is a nitrosyl adduct formed directly in the solid state. Equation 7 represents the reaction of NO gas with a MP in solution, resulting in the formation of MP(NO)(solv), which is the nitrosyl adduct in solution. When drops of the solution are placed onto the CdSe surface under a stream of nitrogen, a film of $MP(NO)(f)_{preformed}$ is deposited. The strikingly different PL sensing capabilities of the nitrosyl films prepared by these two methods led us to examine further their properties by solid-state IR and electronic absorption spectroscopy.

A variety of MP films were prepared on CdSe substrates, and their NO binding behavior was studied by IR spectroscopy. NO was bubbled through a CH_2Cl_2 solution of either $Co^{II}TPP$ or $Co^{III}TPPCl$ and the preformed nitrosyl product deposited on the substrate. Figure 6 presents the IR spectrum of a film prepared from $Co^{II}TPP$ in this manner; the same product was formed from both the $Co^{II}TPP$ and $Co^{III}TPPCl$ starting materials, and the spectra obtained matched that of $Co^{II}TPP(NO)$ previously reported.[36]

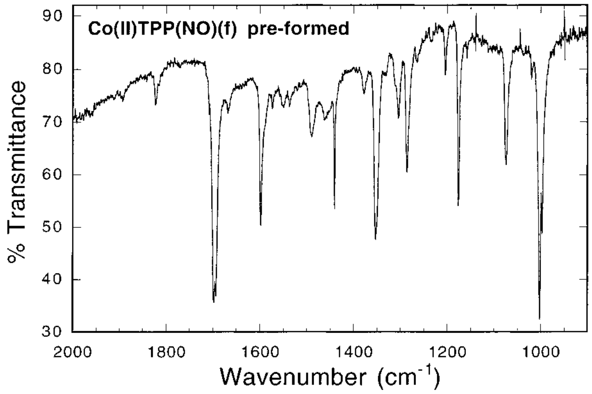

Figure 6. IR spectrum of a film of the nitrosyl adduct of $Co^{II}TPP$, preformed in solution by bubbling excess $^{14}NO(g)$ through a methylene chloride solution of the metalloporphyrin. Drops of this nitrosyl adduct solution were placed onto the semiconductor surface to yield the film of $Co^{II}TPP(NO)_{preformed}$. The spectrum was collected in transmission mode using 200 scans and 1 cm^{-1} resolution. See the Experimental Section for complete conditions for these IR studies. Peaks at 1003, 1260, 1350, 1450, and 1600 cm^{-1} were seen in all IR film spectra of all $Co^{II}TPP$ and $Co^{III}TPPCl$ complexes and have been assigned to ν_{C-H} rock (pyrrole), $\nu_{=N-H}$ in-plane, $\nu_{=C-N}$ stretch, ν_{C-H} bend (pyrrole), and $\nu_{-C=C-}$ (phenyl), respectively. The stretching frequency assignments are based on refs 35, 46, and 47.

Direct formation of the same $Co^{II}TPP(NO)$ adduct was observed in the solid state, when films of either $Co^{II}TPP$ or $Co^{III}TPPCl$ were exposed to gaseous NO (eq 6). Films of Co^{II}-TPP and $Co^{III}TPPCl$ were also deposited directly from solution and subsequently exposed to either ^{14}NO or ^{15}NO. The peak positions of the bulk films of $Co^{II}TPP$ and $Co^{III}TPPCl$ were the same as those previously reported for these complexes;[36,49,50] thus, the metalloporphyrin in the bulk film appears unaffected by the semiconductor substrate. When the films of $Co^{II}TPP$ and $Co^{III}TPPCl$ were exposed to ^{14}NO, a new peak appeared at approximately 1700 cm^{-1}. The assignment of this peak to ν_{NO} was verified by isotopic substitution; when ^{15}NO was substituted for ^{14}NO, the film exhibited a peak at approximately 1670 cm^{-1} (Figure 7 and Table 3). The spectrum obtained when a film of either $Co^{II}TPP$ or $Co^{III}TPPCl$ was exposed to ^{14}NO (eq 6) matched that of a $Co^{II}TPP(NO)_{preformed}$ film (eq 7), suggesting that the same chemistry occurs in the bulk film as in solution. Since films of $Co^{II}TPP(NO)$ do not mediate a PL response to NO, and the formation of $Co^{II}TPP(NO)$ in the bulk film appears irreversible, the bulk chemistry cannot account for the observed reversible PL response of $Co^{III}TPPCl$ films to NO.

For comparison with the $K_{interface}$ values, we attempted to estimate the equilibrium constant for uptake of nitric oxide by the bulk metalloporphyrin film, K_{film}, using IR spectral changes, as described previously.[21] Coatings of $Fe^{III}TPPCl$ or $Co^{III}TPPCl$ were placed onto a large CdSe crystal, and the spectral changes in the ν_{NO} spectral region were monitored as a function of NO partial pressure. The conversion was monitored at ν_{NO} = 1700 cm^{-1}, and several different films were used to monitor the NO uptake by the MP-coated surface. Due to the decaying current from the synchrotron source, we were unable to obtain accurate

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(49) Thomas, D. W.; Martell, A. E. *J. Am. Chem. Soc.* **1959**, *81*, 5111.

(50) Shimomura, E. T.; Phillippi, M. A.; Goff, H. M.; Scholz, W. F.; Reed, C. A. *J. Am. Chem. Soc.* **1981**, *103*, 6778.

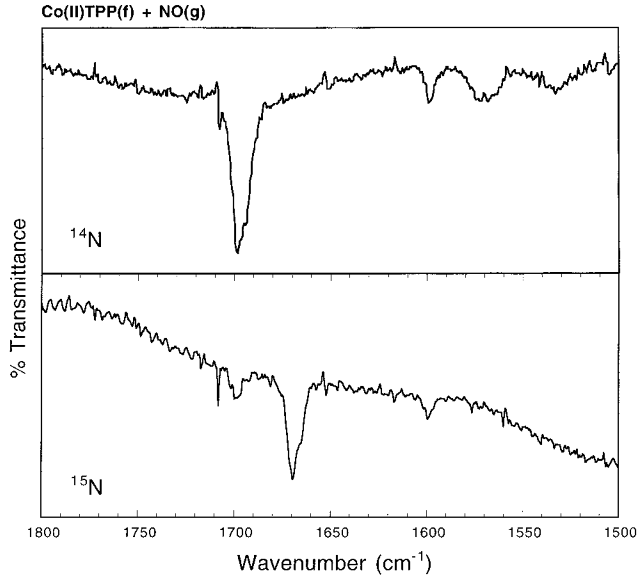

Figure 7. IR spectra comparing the ν_{NO} region of films of $Co^{II}TPP$ that were exposed to $^{14}NO(g)$ and $^{15}NO(g)$ to form directly the nitrosyl adduct in the solid state. The two spectra were collected under identical conditions in transmission mode using 200 scans and 1 cm^{-1} resolution, using two different samples.

Table 3. IR Results for Films[a]

film	ν_{NO} (cm^{-1})
$Co^{II}TPP(f)$[b] {direct}	
$Co^{II}TPP(f) + {}^{14}NO(g)$[c] {direct}	1700
$Co^{II}TPP(f) + {}^{15}NO(g)$[d] {direct}	1670
$Co^{II}TPP(solv) + {}^{14}NO(g)$[e] {preformed}	1700
$Co^{III}TPPCl(f)$[b] {direct}	
$Co^{III}TPPCl(f) + {}^{14}NO(g)$[c] {direct}	1698
$Co^{III}TPPCl(f) + {}^{15}NO(g)$[d] {direct}	1668
$Co^{III}TPPCl(solv) + ({}^{14}NO)$[e] {preformed}	1700

[a] The spectra were collected in transmission mode using 200 scans and 1 cm^{-1} resolution. [b] The film was evaporated onto the surface of the single-crystal CdSe, as described in the Experimental Section, from a methylene chloride solution of the indicated metalloporphyrin under strictly anaerobic conditions. [c] The metalloporphyrin film was prepared as described in footnote *b* and subsequently exposed to a flow of $^{14}NO(g)$ for at least 3 min. The container was subsequently purged with dry nitrogen to eliminate the excess $^{14}NO(g)$. [d] The film was prepared as described in footnote *c*, except that $^{15}NO(g)$ generated in situ was used (see the Experimental Section for $^{15}NO(g)$ generation procedure). [e] The nitrosyl adduct of either $Co^{III}TPPCl$ or $Co^{II}TPP$ was preformed in solution by bubbling excess $^{14}NO(g)$ through a methylene chloride solution of the metalloporphyrin; the film was then prepared by solvent evaporation (see Experimental Section and the text).

estimates of K_{film} by this method. However, we can infer that values for K_{film} are considerably higher than corresponding $K_{interface}$ values due to the complete conversion to a nitrosyl adduct observed by IR at much lower partial pressures (<0.02 atm) than observed during the PL measurements (typically ~1 atm). For the FeTPPCl case our experimental setup did not allow us to create sufficiently low NO concentrations to determine at what pressures of NO the adduct begins to form and saturate.

Solid-state electronic absorption spectroscopy was also used to track the binding of NO to the MP films. As described in the Experimental Section, a solution of FeTPPCl or CoTPPCl was evaporated onto a quartz cuvette and subsequently repeatedly exposed to various pressures of NO in a sealed container. As represented in Figure 8, a substantial red shift of the most intense absorption peak was observed for all complexes, indicating the formation of a nitrosyl adduct; the lack of an isosbestic point suggests that multiple species and/or binding environments may be involved. The onset of the spectral changes was observed at very low pressures of NO, similar to those used for the IR studies, indicating that the binding profiles observed by solid-state IR and solid-state electronic spectroscopy are similar. Due to the complexity of the spectral changes, we are unable to estimate *K* values directly from these data. However, a substantial difference between interface and film binding affinities is highlighted in Figure 9, which directly compares the concentration profiles of the UV−vis and PL measurements for films of $Co^{III}TPPCl$. Especially noteworthy is the saturation of response seen by PL at roughly a 10-fold higher concentration than is observed by UV−vis or IR spectroscopy. On the basis of this comparison we can estimate that there is on the order of at least a 10-fold preference for NO to bind in the bulk film rather than at the buried semiconductor−film interface.

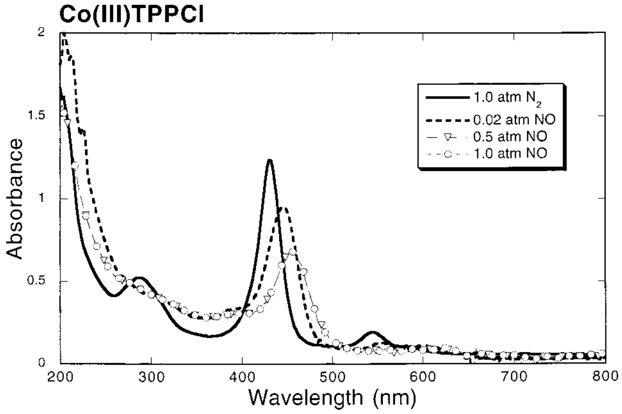

Figure 8. Solid-state UV−vis spectra on a quartz slide illustrating the spectral changes of a film of $Co^{III}TPPCl$ exposed to increasing pressures of $^{14}NO(g)$. The film preparation procedure and gas handling apparatus are described in the Experimental Section.

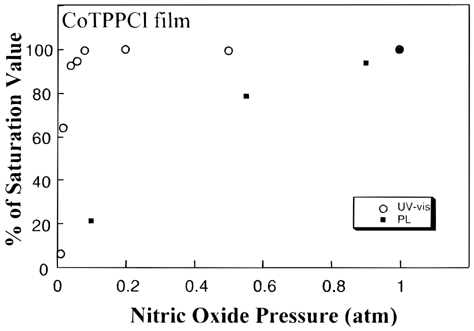

Figure 9. Normalized UV−vis responses (circles) of a film of Co^{III}-TPPCl on a quartz cuvette and of PL responses (squares) of a film of $Co^{III}TPPCl$ on CdSe to changes in NO partial pressure. Responses were normalized so that the UV−vis absorption (monitored at 431 nm) and PL intensity changes at the saturation level were both set to 100%; intermediate values are expressed as percentages of the saturation value.

IV. Binding Characteristics. Metalloporphyrins have documented ability to coordinate several different ligands to their metal centers.[51] In a nitrogen-saturated solution, the M(III) center in the MP acts like a Lewis acid, causing a quench in the PL intensity relative to nitrogen-saturated methylene chloride solution. When nitric oxide saturated solutions were used, a nitrosyl adduct of each MP was generated, and a Lewis basic PL response was observed. We believe that the difference in the PL response in solution between the two ambients is most

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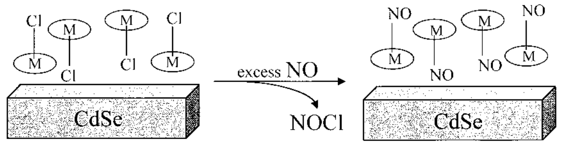
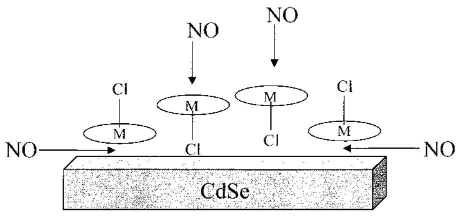
(51) Bertini, I.; Gray, H. B.; Lippard, S. J.; Valentine, J. S. *Bioinorganic Chemistry*; University Science Books: Sausalito, CA, 1994.



A. Solution Scheme



B. Film Scheme

Figure 10. Idealized representation of the possible binding modes of MTPPCl in the solution and solid state with nitric oxide.

likely due to a change in the coordination environment around the metal center due to the formation of a nitrosyl adduct, as postulated in Figure 10A. This irreversible change once NO is introduced causes the analyte to donate additional electron density to the bulk of the semiconductor, thereby shrinking the depletion region and enhancing the PL intensity.[19]

The PL effects observed in the solid state are quite different from the solution effects. The introduction of nitric oxide into the ambient around the coated semiconductor resulted in reversible PL changes. This observation is suggestive of the formation of a weak nitrosyl adduct, that is readily dissociated once NO is removed from the system, as depicted in Figure 10B. The proposed chemistry in the bulk film is given by eq 8.

$$\mathrm{MTPPCl(f)} + \mathrm{NO(g)} \leftrightarrow \mathrm{MTPPCl(NO)(f)} \qquad (8)$$

Assembled MP arrays have been shown under certain conditions to accommodate a variety of hosts,[28] and therefore it is not surprising that solid MTPPCl on CdSe can bind NO from the gas phase. However, all of the PL data collected suggests that the nitrosyl adduct formed at the semiconductor−film interface is different from that preformed in solution or in the bulk film. Our reversible PL changes in the solid state lead us to the conclusion that nitric oxide participates in some kind of adduct interaction with the metalloporphyrin that is uniquely mediated by the presence of the semiconductor surface. The IR film data in Table 3 indicate that there is no difference between the nitrosyls prepared by the two different methods (direct and preformed).

The porphyrins present at the semiconductor−film interface may be sterically restricted, and the unique environment of the interfacial region may alter the chemistry observed when NO is present. Although the bulk porphyrin may undergo reduction by NO, with concomitant release of NOCl, similar reaction of the porphyrin at the interface may be inhibited. Under such conditions, binding of NO to the $\mathrm{Co^{III}TPPCl}$ provides a plausible mechanism for the reversible PL response observed, as illustrated schematically in Figure 10B, with structure as shown in Chart 1C. Alternatively, $\mathrm{Co^{II}TPP(NO)}$ may indeed form, but the nitrosyl adduct may be subject to destabilizing steric or electronic effects at the film−semiconductor boundary. The data presented herein reveal that the interaction between NO and the porphyrin is mediated by the presence of the surface atoms on the semiconductor crystal, weakening the binding of NO at the interface. The lowered affinity of the porphyrin at the film−semiconductor interface is presumably responsible for the reversible PL response. Further experimentation using other surface-sensitive techniques may provide additional details as to the nature of the adduct formed at the interface.

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