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Detection of Chiral Analytes through Adduct Formation with Chiral Films Coated onto Emissive Cadmium Selenide Substrates

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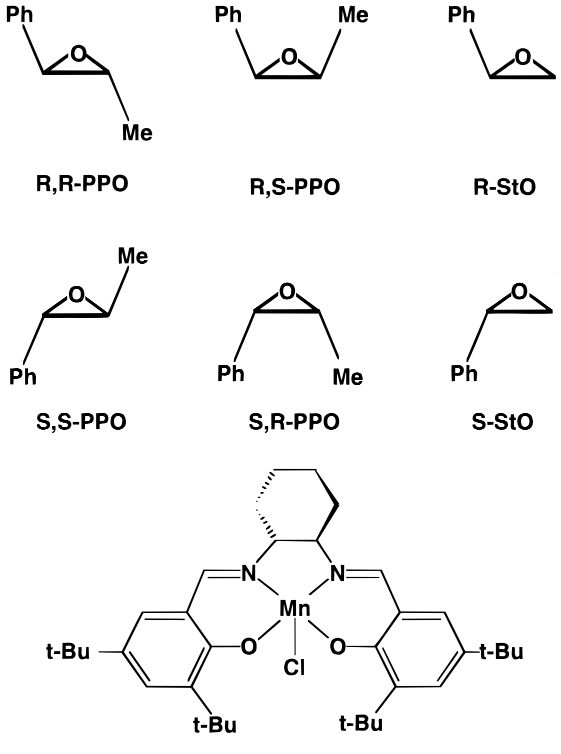
Abstract: A film of [*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine]manganese(III) chloride, **1**, adsorbed onto an n-type CdSe single-crystal substrate acts as a stereoselective transducer for chiral analytes, coupling the complexation chemistry of the film to the band gap photoluminescence (PL) intensity of the underlying semiconductor. Exposure of the uncoated semiconductor to phenylpropylene oxide (PPO) and styrene oxide (StO) vapor results in a small PL enhancement relative to a vacuum reference level that is the same within experimental error for the four PPO and for the two StO stereoisomers. In contrast, exposure of the coated semiconductor to PPO and StO vapor substantially enhances the CdSe PL intensity relative to its intensity under vacuum conditions, and the optical response is stereoselective, with the PL enhancements and equilibrium adsorption constants dependent on the chirality of both the adsorbate and film. Use of a *S*,*S*-**1** film on CdSe gives larger PL enhancements and equilibrium binding constants (estimated using the Langmuir adsorption isotherm model) for *S*,*S*,-PPO, *R*,*S*-PPO, and *R*-StO than for the enantiomer of each of these epoxides. When the *R*,*R*-**1** film is employed on CdSe, the expected enantiomeric relationship is observed, with *R*,*R*-PPO, *S*,*R*-PPO, and *S*-StO yielding larger PL enhancements and equilibrium binding constants. Binding constants for the preferred film−analyte interactions are in the range of 10^3 to 10^4 atm^{-1}. The PL enhancements can be fit to a dead-layer model, except at short wavelengths where evidence for photodissociation of the epoxide from the film is obtained, and maximum reductions in depletion width caused by epoxide−film adduct formation are estimated to range from ∼200 to 800 Å. The PL response can in principle serve as the basis for an on-line chemical sensor for chiral analytes.

Introduction

The use of chiral metal complexes to catalyze stereoselective syntheses is attracting considerable interest.[1] For example, Jacobsen et al. have described the use of the chiral manganese salen complex, [*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine]manganese(III) chloride (**1**, shown in Figure 1), as a catalyst for the enantioselective synthesis of chiral epoxides by the asymmetric epoxidation of alkenes with bleach.[2−5] By adjustment of the reaction conditions and the chirality of the manganese complex, each of the four stereoisomers of phenylpropylene oxide (PPO), shown in Figure 1, can be produced as the dominant product of this reaction;[2,3] with less selectivity, either of the two styrene oxide (StO) isomers shown in Figure 1 can be produced.[4]



R,R-1

Figure 1. Structures of the Jacobsen catalyst, **1**, and the stereoisomers of the phenylpropylene oxide (PPO) and styrene oxide (StO) analytes.

Probes of the complexation chemistry underlying these reactions could be valuable in characterizing such catalysts and in the design of new catalysts. Moreover, adduct-forming reactions of the catalyst can in principle provide a simple inexpensive method for monitoring, in real time, the stereochemical evolution of a reaction mixture that could be useful for optimizing reaction variables. At present, the composition of such mixtures is typically analyzed by sampling with chromatography and NMR spectroscopy, using chiral columns and shift reagents.[6−9]

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We demonstrate in this paper that films of chiral metal complexes coated onto emissive semiconductor substrates can serve as stereospecific transducers: Chiral analytes can cause stereospecific, reversible changes in the photoluminescence (PL) intensity of the coated substrate. These PL signatures can be used to characterize the strength of adducts formed between the analyte and the compound comprising the film and to serve as the basis for on-line detection of these species.

We have previously shown that the band gap PL intensity of single-crystal II−VI semiconductors such as n-CdSe can be perturbed reversibly by molecular adsorption relative to the PL intensity in a reference ambient, often nitrogen gas or vacuum.[10] Underpinning this effect is the modulation, by adsorption, of the electric field thickness, the depletion width, in the near-surface region of the semiconductor. A dead-layer model has been used to quantify these effects; this model assumes that photogenerated electron-hole pairs created in a thickness on the order of the depletion width are separated by the electric field and do not contribute to PL intensity.[11,12] Adsorption of Lewis bases causes electron density to shift from the surface toward the bulk solid, decreasing the depletion width and enhancing CdSe PL intensity; in contrast, adsorbed Lewis acids shift electron density from the bulk toward the surface, quenching PL intensity. These effects define a kind of "luminescent litmus test" that may serve as the basis for optically-based chemical sensors.

We have recently demonstrated that this methodology can be extended by coating the semiconductor with a film of a metal complex having a strong affinity for the surface and the ability to bind a targeted analyte reversibly. For example, a cobalt salen complex coated onto n-CdSe was shown to act as a dioxygen-driven transducer: Reversible dioxygen-induced quenching of PL intensity was observed relative to a nitrogen reference ambient.[13]

In this paper we demonstrate that chiral analytes can be detected in the vapor phase by coating emissive single-crystal, etched n-CdSe substrates with chiral films of **1**. Specifically, we observe PL intensity enhancements of the **1**-coated semiconductors that depend both on the chirality of the film and the particular stereoisomer of PPO and StO to which it is exposed. These experiments demonstrate that the chiral complex **1** serves as a versatile ligand-binding platform that links film complexation chemistry to the substrate's electronic structure.

Experimental Section

Materials. Single-crystal, vapor-grown c-plates of n-CdSe, having a resistivity of ∼2 Ω·cm, were obtained from Cleveland Crystals, Inc. These crystals were polished with alumina powder (Buehler; 5 μm) and then sonicated in methanol. The n-CdSe samples were then etched with 1:15 v/v Br_2/MeOH for 20 s, revealing the shiny Cd-rich (0001) face that was illuminated in these PL experiments. The *R*,*R*- and *S*,*S*-Jacobsen catalyst (98%), (*R*,*R*)- and (*S*,*S*)-phenylpropylene oxide (98%; 99% ee), and (*R*)- and (*S*)-styrene oxide (98%) were purchased from Aldrich; the liquids were vigorously deoxygenated by repeated freeze, pump, and thaw cycling, but otherwise used as received. Methylene chloride (Aldrich; 99+% with H_2O < 0.005%) was distilled over calcium hydride under nitrogen immediately before use.

Synthesis of (*R*,*S*)- and (*S*,*R*)-Phenylpropylene Oxide. The *cis*-phenylpropylene oxides were prepared by a modified literature procedure.[2,14] In a typical synthesis, 1.0 g of 1-phenyl-1-propyne (Aldrich; 99%) was injected into a round-bottom flask containing ∼20 mL of deaerated pentane (VWR Scientific; 98%; distilled over Na, under N_2) and 1.0 g of Lindlar catalyst (Pd/$CaCO_3$ poisoned with Pb; Aldrich). Hydrogen gas (Liquid Carbonic Specialty Gas Corporation; 99.9%) was periodically bubbled through the flask (about 200 mL once per hour), and the reaction mixture was stirred for 8 h. Nearly quantitative yields of *cis*-phenylpropene were isolated by rotary evaporation of the solvent, followed by distillation of the product. Stirring ∼0.50 g of *cis*-phenylpropene in a diluted, buffered, aqueous solution of bleach (Clorox diluted to 0.55 M NaOCl with 0.05 M Na_2HPO_4; pH adjusted to 11.3 with the addition of 1 M NaOH) and R,R-**1** for 6 h with an ice bath yielded ∼0.10 g of (*R*,*S*)-phenylpropylene oxide, isolated by column chromatography through alumina (Fisher Scientific) with 5% (v/v) CH_2Cl_2 in pentane as eluting solvent. Reaction with *S*,*S*-**1** gave a similar yield of the *S*,*R*-epoxide. The identity and purity of the products were confirmed with ^{1}H NMR.[2] The enantiomeric excess of ∼80−90% was confirmed by ^{1}H NMR with the addition of the chiral resolving reagent tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]europium(III) (Aldrich; 98%).

Film Preparation. The films of **1** were deposited by dipping the mounted (see below) semiconductor samples, previously etched as described above, in concentrated HCl for 10 s, rinsing with MeOH, then adding 5 drops of 1 mM methylene chloride solution of **1** to the (0001) face of the samples. The solvent was evaporated under a dry nitrogen stream, and the sample then quickly transferred to the vacuum line. Alternately, the n-CdSe crystals were dipped in the **1** solution for 10 min following the HCl treatment, then rinsed and mounted. For both film applications, the acid pretreatment was required to produce coated samples that exhibited a PL response upon exposure to the analyte gases.

Apparatus. The PL sample cell consisted of an outer glass tube of 20-mm inner diameter, sealed at one end and connected by ground glass seal with a Viton O-ring to an inner glass tube (i.d. 6 mm) at the other end. The semiconductor sample was mounted on the outside of the 6-mm glass tube with Teflon supports. The analyte liquids were contained within glass bulbs with Teflon stopcocks. The sample cell and analyte bulbs were connected to a stainless steel gas-handling system and vacuum line with Cajun Ultra-Torr fittings. Gas pressures inside the system were measured with a set of MKS Instruments Baratron capacitance manometers. The gas-handling system was wrapped in resistive heating tape and maintained at a constant temperature of 313 K throughout the gas phase experiments; the experiments were conducted at this elevated temperature in order to provide adequate vapor pressure for the analytes examined. The elevated temperature did not appear to adversely affect the films: Based on the PL response, no degradation was observed for films of **1** over the course of experiments lasting for up to 8 h at 313 K.

Optical Measurements. Electronic absorption spectra were obtained with a Cary 17D spectrophotometer. For PL measurements, a Coherent Innova 90-5 3.0-W Ar^+ laser was used for 458- 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 Oriel Instaspec II systems. Laser light intensities were measured with a Coherent Model 212 power meter. For these gas-phase experiments, the red band-edge PL of n-CdSe was monitored at the band maximum of ∼720 nm while the semiconductor sample was under vacuum or exposed to 10^{-4} to 10^{-1} atm of analyte vapor. Changes in the analyte pressure were carried out by evacuating the gas line to 10^{-6} atm and refilling with vapor from an attached analyte bulb.

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(8) Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; John Wiley and Sons: New York, 1994.

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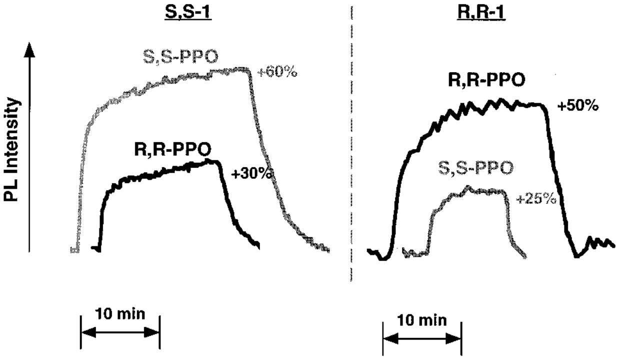

Figure 2. Changes in the PL intensity of n-CdSe samples coated with *S,S*-**1** on exposure to the same pressure (3.9×10^{-4} atm; 0.30 Torr) of *trans*-PPO isomers shown in Figure 1. One n-CdSe sample and film was used for the measurement of the PL response to two enantiomers of *trans*-PPO. The film was then removed, the crystal re-etched, and a new film of *R,R*-**1** used for the measurement of the same analytes. In all of these experiments, the PL was excited by 633-nm light (~40 mW/cm^2), and PL intensity was monitored at 720 nm. The start of each trace indicates the vacuum reference level (~10^{-6} atm).

Results and Discussion

Photoluminescence Experiments. Samples of etched, single-crystal n-CdSe emit red band-edge PL (the band gap energy, E_g, is ~1.7 eV with λ_{max} ~720 nm) when excited with ultraband gap light. When the ambient, at 313 K, surrounding an n-CdSe semiconductor crystal is switched from vacuum to PPO or StO vapor, the intensity of the band edge photoluminescence, excited by 633-nm radiation, increases with analyte pressure up to a maximum enhancement of only ~5 to 10%, relative to the vacuum reference level. In pairwise comparisons, identical PL enhancements within experimental error were observed for similar pressures of both enantiomers of *cis*-PPO, *trans*-PPO, and StO. Because the PL spectral distribution at low resolution (~0.5 nm) was unaffected by adsorption of the analytes, PL intensity changes were monitored exclusively at the band-edge PL maximum.

We have interpreted semiconductor PL intensity enhancements as arising from the formation of a surface charge-transfer complex with a Lewis base;[10,15] as noted above, adsorption of the base can shift electron density from surface states back into the bulk solid, decreasing the depletion width and enhancing PL intensity. A possible binding scenario might be that the oxygen atom of the epoxide can serve as an electron donor toward coordinatively unsaturated surface Cd sites.

Etched samples of CdSe coated with a film of the chiral complex **1** exhibit substantially larger maximum PL intensity enhancements in the presence of the epoxides, as compared with the uncoated samples. As illustrated in Figure 2 and summarized in Table 1, under identical excitation conditions, the n-CdSe PL intensity was routinely enhanced by a maximum of ~20 to 90% relative to the vacuum reference level. This is consistent with an increase in the film's basicity toward the underlying semiconductor surface, which could occur, for example, by ligation of the epoxide oxygen atom to the Mn atom.

Figure 2 also reveals the PL responses to be enantioselective: Exposure of a n-CdSe sample coated with a film of *S,S*-**1** to identical pressures of the two *trans*-PPO isomers results in a substantially larger relative PL enhancement for *S,S*-PPO than for *R,R*-PPO. The expected film–analyte enantiomeric relationship is observed: When the chirality of the film is reversed to *R,R*-**1**, a greater PL enhancement is produced by *R,R*-PPO than by *S,S*-PPO. Similar effects are observed for exposure of **1**-coated CdSe to the enantiomers of *cis*-PPO, with the *S,S*- and *R,R*-**1** films giving larger PL enhancements with *R,S*-PPO and *S,R*-PPO, respectively. Figure 3 illustrates the maximum fractional PL intensity enhancements for exposure of CdSe to all four PPO isomers, in the absence of a film of **1** and in the presence of *R,R*- and *S,S*-**1** films.

Table 1. PL Properties of Film–Analyte Structures

film/analyte[a]	% ΔPL[b]	Δ*D*,[c] Å	*K*,[d] atm^{-1}
S,S-**1** film			
R,R-PPO	28	310 ± 20	<1000
***S,S*-PPO**	41	**430 ± 20**	**5400 ± 1200**
***R,S*-PPO**	89	**800 ± 40**	**1900 ± 100**
S,R-PPO	58	570 ± 30	340 ± 30
***R*-StO**	92	**820 ± 40**	**4200 ± 500**
S-StO	49	500 ± 30	1600 ± 30
R,R-**1** film			
***R,R*-PPO**	89	**800 ± 40**	**15000 ± 2000**
S,S-PPO	47	490 ± 30	<1000
R,S-PPO	31	340 ± 20	370 ± 90
***S,R*-PPO**	44	**460 ± 30**	**1100 ± 70**
R-StO	18	210 ± 10	2900 ± 300
***S*-StO**	36	**390 ± 20**	**11000 ± 200**

[a] Single-crystal n-CdSe samples coated with the indicated isomer of **1** were exposed to the indicated epoxide analyte isomer in the gas phase. The PL experiments were run in pairs, with both enantiomers exposed to the same film-coated sample. Bold type is used to highlight the preferred interaction in each pair of enantiomers. All data were obtained at 313 K, with excitation at 633 nm, using an intensity of 40 mW/cm^2. [b] Percentage PL enhancements at saturation relative to the vacuum reference ambient. [c] Dead-layer contractions, Δ*D*, corresponding to the percentage PL enhancements in the preceding column. These values are calculated using eq 1. Uncertainties shown are for the particular measurement. The error bars reflect the error of less than or equal to 5% in the measurements reported in the previous column. [d] Estimated equilibrium binding constants for the adsorption of the indicated epoxide onto the coated substrate; these values are obtained from PL changes and eq 3, as described in the text. Uncertainties shown are for the particular measurement. Upper-limit values for some film–analyte combinations reflect systems for which the PL changes had not saturated under our experimental conditions.

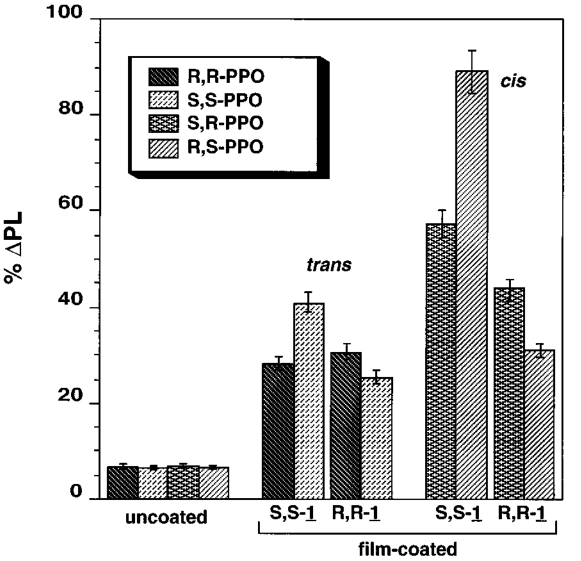

Figure 3. Comparison of percentage PL enhancements at saturation induced by exposure of uncoated and *R,R*-**1**- and *S,S*-**1**-coated CdSe to the four PPO isomers. The same film of *R,R*-**1** and *S,S*-**1** was used for these direct comparisons, but these were different film samples than those of Figure 2. Excitation conditions are as given for Figure 2.

While the PL enhancement observed for binding *S,S*-PPO to the *S,S*-**1** film should theoretically be identical to that observed

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for binding *R*,*R*-PPO to the *R*,*R*-**1** film (likewise for other enantiomeric combinations involving films of **1** with the *R*,*S*- and *S*,*R*-PPO isomers, and with the *R*- and *S*-StO isomers), the observed differences highlight, we believe, film-to-film variations that can be expected from the crude etching and coating procedures employed (compare, e.g., the maximum PL enhancements for the *trans*-PPO isomers in Figures 2 and 3). Binding constants (vide infra and Table 1) reflect these film-to-film variations, as well. However, the selectivity of PL responses upon exposure of the **1**-coated CdSe to enantiomeric pairs of epoxides was routinely reproduced between film preparations. Moreover, for a given film the experiments were routinely conducted multiple times to establish reproducibility. The variation in PPO isomer response for a given film could reflect different absolute coverage of the adsorbates, differences in the sites used for adsorption, and/or differences in ligation at a given site.

Dead-Layer Model. The amount of PL enhancement induced by the adsorption of gaseous analytes on the coated or uncoated n-CdSe surface can be treated quantitatively using the aforementioned dead-layer model, which assumes that the near-surface region of the semiconductor that supports the electric field is nonemissive. The quantitative form of the dead-layer model is given by eq 1,[10]

$$\mathrm{PL_x/PL_{ref}} = \exp(-\alpha' \Delta D) \qquad (1)$$

where $\mathrm{PL_{ref}}$ is the PL intensity in the vacuum reference ambient; $\mathrm{PL_x}$ is the PL intensity in the presence of the adsorbing epoxide isomer; $\alpha' = (\alpha + \beta)$ is the sum of the semiconductor absorptivities for exciting and emitted light;[16] and $\Delta D = (D_x - D_{\mathrm{ref}})$ 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 τ are the minority carrier diffusion length and lifetime, respectively), both in the absence and presence of the adsorbate.[17]

Values of ΔD derived from PL experiments that are independent of excitation wavelength (458, 514, and 633 nm) are in agreement with the dead-layer model.[18] For uncoated samples, a good fit to the model was found, yielding a value of ΔD of ~100 Å, independent of the PPO and StO isomer employed as the adsorbate.

After coating the CdSe sample with a film of either *S*,*S*-**1** or *R*,*R*-**1**, the PL enhancements induced by PPO and StO isomers under the same excitation conditions still fit the dead-layer model with 514- and 633-nm interrogating wavelengths and yielded larger values of ΔD ranging from ~200 to 800 Å. However, ΔD values calculated from experiments using 458-nm excitation were invariably smaller, an effect that can be attributed to photoinduced desorption of the PPO and StO at this shorter wavelength.[19] Table 1 lists the calculated dead-layer contractions observed for the exposure of both the **1**-coated semiconductor samples to the PPO and StO isomers.

The reduction in semiconductor surface charge accompanying the formation of the ligand−film adducts can be calculated from eq 2,[20]

$$\Delta w = \Delta N_s / |(N_d - N_a)| \qquad (2)$$

where Δw is the change in the depletion width; $\Delta N_s = (N_{s,x} - N_{s,\mathrm{ref}})$ is the change in the density of negative surface charge; and N_a and N_d are the densities of acceptor and donor atoms in the semiconductor, respectively. Use of eq 2 assumes that the calculated contraction in depletion width is equal to the reduction in the dead-layer thickness. Based on the resistivity and the lattice constant for these wurtzite samples,[21,22] surface charge reductions on the order of less than one per ten thousand surface atoms result in easily measurable changes in PL intensity. This low value may reflect the morphology of the coatings. If uniform coverage resulted from the coating procedure, a film of ~0.1 μm in thickness would result. We suspect that uneven morphologies, including islands, are produced and that it is the PPO adsorbed at molecules of **1** most proximate to the semiconductor surface that leads to PL changes.

Langmuir Adsorption Isotherm Model. The concentration dependence of the PL enhancements can be used to estimate the equilibrium constant for surface adduct formation with the Langmuir adsorption isotherm model. The quantitative form of the model is given by eq 3,[23]

$$\Theta = KP/(1 + KP) \qquad \text{or} \qquad 1/\Theta = 1 + (1/KP) \qquad (3)$$

where Θ is the fractional surface coverage for active binding sites; K is the equilibrium constant for surface adduct formation; and P is the pressure of the uncomplexed epoxide. Values of Θ are estimated as the fractional changes in the dead-layer thickness occurring between the reference vacuum ambient ($\Theta = 0$) and the saturated PL enhancement, $\mathrm{PL_s}$, which is assumed to correspond to the complete coverage of active surface adsorption sites ($\Theta = 1$). At intermediate values of PL intensity, $\Theta = [\ln(\mathrm{PL_x/PL_{ref}})/\ln(\mathrm{PL_s/PL_{ref}})]$.

Figure 4 shows representative data for the adsorption of *R*,*S*- and *S*,*R*-PPO onto the (0001) face of n-CdSe coated with *S*,*S*-**1**. Best fits to the Langmuir adsorption isotherm model yield equilibrium adsorption constants K of ~10^2−10^4 atm^{-1} for a variety of coated n-CdSe samples.[24] Table 1 lists the binding constants found for adsorption of the analytes of interest onto CdSe samples coated with *S*,*S*-**1** and *R*,*R*-**1**. With the *S*,*S*-**1** coating, the largest value of K , ~5000 atm^{-1}, is found with *S*,*S*-PPO, and its enantiomer, *R*,*R*,-PPO, yields a substantially smaller value of <1000 atm^{-1}; acquisition of a more accurate value was precluded by the inability to attain the saturated PL intensity under our experimental conditions. Likewise, there

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(16) Parsons, R. B.; Wardzynski, W.; Yoffe, A. D. *Proc. R. Soc. London, Ser. A.* **1961**, *262*, 120.

(17) (a) Mettler, K. *J. Appl. Phys.* **1977**, *12*, 75. (b) Burk, A. A., Jr.; Johnson, P. B.; Hobson, W. S.; Ellis, A. B. *J. Appl. Phys.* **1986**, *59*, 1621.

(18) Absorptivities for CdSe span a factor of roughly 3 for these three wavelengths.

(19) An optical absorption spectrum for a film of **1** deposited on a quartz slide from methylene chloride solution revealed that 458-nm light is strongly absorbed relative to 514- and 633-nm light. The observed photoeffects are consistent with the notion that photoinduced desorption of the epoxide ligand occurs when the coated semiconductor samples are probed with 458-nm light: Fractional PL enhancements and thus ΔD values were unaffected by the excitation intensity with 514- and 633-nm irradiation over a range of 5 to 40 mW/cm^2, but greater fractional PL enhancements (corresponding to larger ΔD values) were observed when the incident intensity was decreased for 458-nm excitation, yielding increasingly satisfactory agreement with the dead-layer model. This is consistent with the notion that lower incident intensities of 458-nm light would permit larger steady-state concentrations of adsorbed epoxide if photodesorption were occurring. A similar effect was seen with dioxygen-induced PL quenching from films of a Co salen complex.[13] Excitation at short wavelengths is thus potentially useful in facilitating desorption of the analyte from the film.

(20) Cox, P. A. *The Electronic Structure and Chemistry of Solids*; Oxford University Press: Oxford, 1987; p 101.

(21) The CdSe resistivity corresponds to a value for $|N_d - N_a|$ of ~5 × 10^{15} cm^{-3}. If binding of **1** is assumed to occur, e.g., at chalcogen atoms, their surface density on the (0001) face of CdSe is 6.3 × 10^{14} cm^{-2}.[22]

(22) *CRC Handbook of Chemistry and Physics*, 70th ed.; CRC Press, Inc.: Boca Raton, FL, 1989; p E-107.

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

(24) The experimental data were also fit to the linear forms of the Temkin and Freundlich adsorption isotherm models,[23] but significantly higher correlation coefficients were generally obtained for the Langmuir adsorption isotherm model.

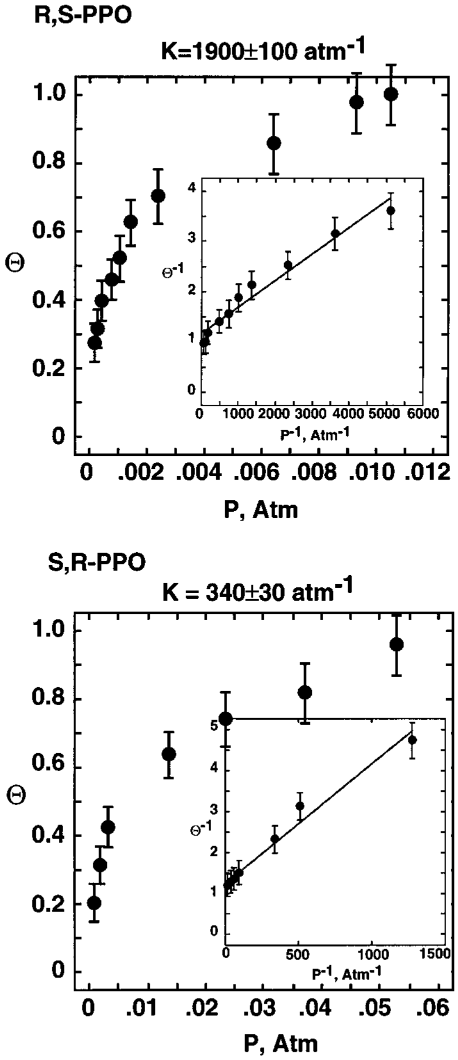

Figure 4. Plots of Θ (assumed to be equal to the fractional dead-layer change resulting from 633-nm excitation) versus pressure for adsorption of *R*,*S*-PPO and *S*,*R*-PPO onto a *S*,*S*-**1**-coated CdSe substrate. Double reciprocal plots of the same data are shown as insets; the linearity of the plots (correlation coefficients 0.98−0.99) represents a good fit to the Langmuir model, and the reciprocal of the slope (eq 3) yields the indicated equilibrium constants *K*.

is roughly a five-fold enhancement in binding constant for *R*,*S*-PPO relative to *S*,*R*-PPO for binding to the *S*,*S*-**1**-coated surface. Use of the enantiomeric *R*,*R*-**1** coating produces an enantiomerically-related ordering of binding constants: substantially larger values of *K* were determined for *R*,*R*-PPO relative to *S*,*S*-PPO, and for *S*,*R*-PPO relative to *R*,*S*-PPO using a common coated substrate. As noted above, the lack of identical binding constants for enantiomerically-related PPO-film combinations presumably reflects film-to-film variations caused by the etching and coating procedures employed. The modest variation in values of *K* for PPO-film combinations likely reflects subtle steric and electronic factors associated with analyte−complex binding in the proximity of the semiconductor surface.

The other chiral analyte examined, StO, mimicked PPO in its PL responses toward the **1**-coated CdSe surfaces, as summarized in Table 1. Specifically, a preference for binding to one of the StO isomers was observed, with the larger value of *K* found for *S*-StO with the *R*,*R*-**1**-coated surface, and for the enantiomerically-related combination of *R*-StO with the *S*,*S*-**1**-coated surface. Interestingly, the StO and *cis*-PPO exhibited the same binding selectivity with respect to the chirality of the phenyl-bearing carbon (see Figure 1), while the *trans*-PPO gave the opposite selectivity, suggesting a sterically determining role for the presence and orientation of the methyl substituent.

Sensor Considerations. The effects of oxygen and water in these experiments are noteworthy. Analyte liquids had to be rigorously deoxygenated, as the presence of oxygen caused a reversible quenching of the PL intensity of the coated substrates relative to the intensity under vacuum. Exposure to water vapor led to slow irreversible PL quenching for the coated and uncoated samples.

Although there are significant practical issues that would need to be addressed before deployment of this particular system would be feasible, the speed of the PL responses illustrated in Figure 2 and their ease of reversibility may lend themselves to the construction of semiconductor PL-based chemical sensor devices.[10] At present, the system is limited by the use of a common PL wavelength for the chiral analytes examined and the modest differences in PL response they elicit. If interfering species can be removed and more discriminating films employed, devices like those described herein could monitor the composition of the headspace above a reaction mixture in real time. The PL responses of CdSe coated with **1** to PPO and StO demonstrate the ability to enantioselectively detect these analytes by coupling the semiconductor PL intensity dependence on surface charge density to film reactivity. The sensitivity of these structures toward PPO and StO extends from ∼10^{-4} to 10^{-1} atm, although, due to the low vapor pressure of these liquids, saturation of the active surface sites with the coated substrates is not achieved for some analytes. Films of chiral metal complexes having different ranges of binding constants may be used to extend the limits of detection in both directions and to quantify gaseous mixtures of these epoxides.

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