

Binding of Fullerenes to Cadmium Sulfide and Cadmium Selenide Surfaces, Photoluminescence as a Probe of Strong, Lewis Acidity-Driven, Surface Adduct Formation

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Abstract: The C₆₀ and C₇₀ fullerenes can be adsorbed from toluene solution onto the surfaces of etched, single-crystal n-CdS and n-CdSe [n-CdS(e)] semiconductors. These fullerene adsorbates act as Lewis acids toward the CdS(e) surface, causing quenching of the solids' band-edge photoluminescence (PL) intensity relative to the intensity in a reference ambient of pure toluene. For C₆₀ adsorbed onto CdSe, the quenching of PL intensity is well fit by a dead-layer model that permits estimation of the adduct-induced expansion in depletion width as being as large as ~300 Å. The degree of quenching is somewhat larger for C₇₀ at a wavelength where the two fullerenes can be directly compared. PL quenching by both fullerenes is concentration dependent and can be fit to the Langmuir adsorption isotherm model to yield large equilibrium binding constants in the range of 10⁵ to 10⁶ M⁻¹; the fullerenes can be detected by this PL method at submicromolar concentrations. Use of the polar Cd-rich (0001) and Se-rich (000 $\bar{1}$) faces of a n-CdSe sample reveals similar binding constants for C₆₀ and C₇₀ on the two faces but larger expansions of the dead-layer thickness from adsorption of either fullerene on the Cd-rich face.

Introduction

The substantial (electro)chemical reduction chemistry of fullerenes and their extensive π systems and unusual steric features intimate the existence of a rich surface coordination chemistry for these remarkable molecules.¹⁻⁴ The recognition and characterization of surface adducts involving C₆₀, C₇₀, and other fullerenes will be a critical element in understanding surface-mediated reactions involving these species.

We have previously shown that the bulk photoluminescence (PL) of certain n-type semiconductors can reveal the presence of adducts formed between molecular species and semiconductor surface atoms. We have interpreted adduct-induced PL changes using a simple model: adsorbing Lewis acids draw electrons from the semiconductor bulk to surface electronic states;⁵ adsorbing Lewis bases push electrons from these states back to the bulk solid.⁶ These shifts in electron density expand (Lewis acids) or

contract (Lewis bases) the electric field thickness, the depletion width, in the solid. The effect can be treated quantitatively with a dead-layer model, which assumes that a region on the order of the depletion width is nonemissive, since photogenerated electron-hole pairs created in this region are separated by the electric field and prevented from radiatively recombining.^{7,8} Lewis acids and bases thus quench and enhance the PL intensity, respectively, relative to a reference medium that lacks the adsorbing species.

In this report we demonstrate that C₆₀ and C₇₀ act as strong Lewis acids toward the surfaces of semiconducting n-CdS and n-CdSe [n-CdS(e)], causing expansions in the dead-layer thickness of hundreds of angstroms. An idealized sketch of fullerene surface coordination to CdS(e) is shown in Scheme I. The fullerenes exhibit large equilibrium binding constants that permit their detection at submicromolar concentrations. Moreover, the PL quenching signature is both fullerene and crystal face dependent: The PL quenching is larger for C₇₀ and for the Cd-rich (0001) face of CdSe (as opposed to the Se-rich (000 $\bar{1}$) face) with both fullerenes.

Experimental Section

Materials. Samples of C₆₀ (Texas Fullerenes Inc., Houston, TX; 99.9+% purity) were used without further treatment; samples of C₇₀ (99+% purity) were kindly provided by Professor Jack Selegue, University of Kentucky, and used as received. Chromatograms confirmed the purity of both fullerenes. Semiconducting n-CdS and n-CdSe samples were vapor-grown, single-crystal, c-plates with a resistivity of ~2 Ω -cm. They were obtained from Cleveland Crystals, Inc. A Br₂/MeOH (1:15 v/v) solution was employed to etch samples. After etching, samples had two

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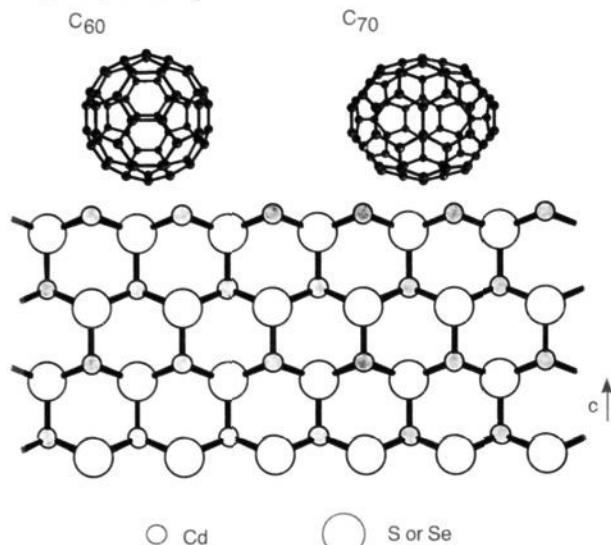
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Scheme 1. Idealized Picture of C₆₀ and C₇₀ Molecules Adsorbed onto the Cd-Rich (0001) Face of a n-CdS(e) Single-Crystal Sample^a



^a The crystallographic *c*-axis lies in the plane of the page, and the Cd-rich and S(e)-rich surfaces used for adsorption studies are perpendicular to the page and are represented by the top and bottom layers of atoms, respectively. The size of the carbon atoms has been reduced for clarity.

visually distinguishable crystal surfaces: a shiny Cd-rich (0001) face and a dull Se- or S-rich (000 $\bar{1}$) face.⁹ The solvent in all studies was N₂-saturated, HPLC-grade toluene (Fisher Scientific).

Apparatus. The semiconductor chip was mounted on a holder, which was a piece of Teflon screwed into an Al extension rod. The rod was lowered into a 7 cm long, 1.8 cm diameter glass tube, the sample cell, through a Teflon adapter, which also served as a stopper for the cell. The glass tube had an inlet tube near the top and a Teflon stopcock at the bottom, which were used for changing the liquid ambient without disturbing the sample-detection optics geometry. The sample cell was kept under a blanket of N₂ and all solutions were saturated with N₂ during experiments.

Optical Measurements. Excitation sources were a Coherent Innova 90-5 Ar⁺ laser (457.9 and 514.5 nm) and a Melles-Griot Model 80 He-Ne laser (632.8 nm). The resulting band edge PL signal of n-CdS(e) ($E_g \sim 1.7$ eV for n-CdSe; $E_g \sim 2.4$ eV for n-CdS) was collected using an optical fiber and measured by a monochromator and PMT as previously described.^{6a} The maximum intensity of the red band-edge emission of n-CdSe was observed at ~ 710 nm, and the maximum intensity of the green band-edge emission of n-CdS was observed at ~ 505 nm. The semiconductor sample was surrounded by a liquid ambient, either pure toluene or a toluene fullerene solution, during the optical measurements. The liquid ambient was switched without moving the sample-detection optics geometry, as described above. The PL response of different crystal faces was examined simply by rotating the etched crystal by 180° to place the opposite polar face in the laser beam.

To ensure that solution absorption effects could be ignored, we estimated the absorbances of 40 μ M C₆₀ and C₇₀ toluene solutions (the maximum concentration used) at the excitation and emission wavelengths employed, using a Hewlett-Packard 8452A diode array spectrophotometer; a 1.0 cm path length cuvette was used to contain the solutions. For the ~ 2 mm path lengths used in the PL experiments, the absorbances for C₆₀ at 458, 515, 633, and 710 nm were all within the instrumental noise (less than 0.01 absorbance units); for C₇₀, only at 633 and 710 nm was the absorbance negligible.

Results and Discussion

Both the red band-edge PL intensity of n-CdSe ($E_g \sim 1.7$ eV; $\lambda_{\max} \sim 710$ nm) and the green band-edge PL intensity of n-CdS ($E_g \sim 2.4$ eV; $\lambda_{\max} \sim 505$ nm) are affected by the adsorption of the C₆₀ or C₇₀ fullerenes onto the surfaces of these CdS(e)

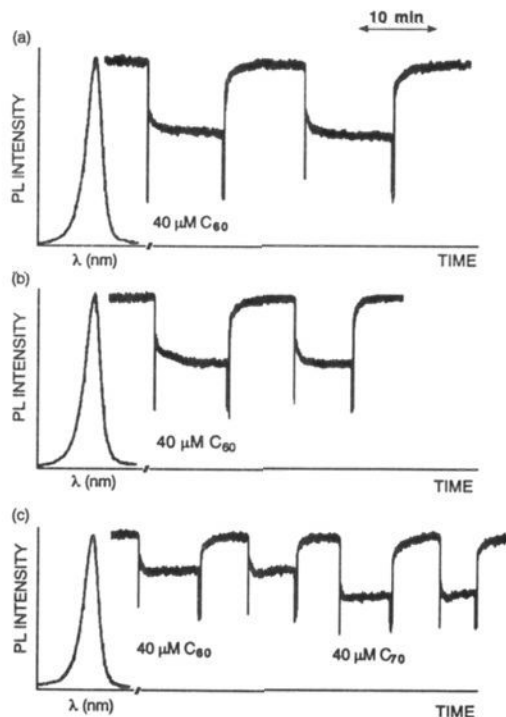


Figure 1. The PL properties of an etched, single-crystal n-CdSe sample [the Cd-rich, (0001) face is exposed to the exciting light], resulting from alternating exposure to pure toluene and a 40 μ M solution of C₆₀ or, right-hand portion of the bottom panel, C₇₀. At the left-hand edge of each panel is the complete emission spectrum, obtained with exciting wavelengths of (a) 457.9, (b) 514.5, and (c) 632.8 nm in pure toluene. Subsequent data in each panel were obtained by monitoring the PL intensity at the emission band maximum of 710 nm and alternating the exposure to pure toluene and the indicated toluene fullerene solution. Two successive trials are shown at each excitation wavelength. The downward spikes are transients that result from the switching of liquid ambients. The fullerene concentrations correspond to saturated PL changes.

substrates. In sections below, we discuss the dependence of adduct-induced changes in electric field thickness on fullerene identity and crystal face and estimate equilibrium binding constants for the adducts.

PL Quenching and the Dead-Layer Model. Figure 1 displays the PL emission band of CdSe in pure toluene and its quenching, relative to pure toluene and monitored at the band maximum of 710 nm, by adsorption of C₆₀ and C₇₀ from toluene solution. Panels a, b, and c of Figure 1 show that the fractional quenching increases with shorter excitation wavelengths. The expedient of monitoring PL changes at the band maximum could be employed because there is no change in the spectral distribution with quenching under the low-resolution conditions employed. Reversibility is also apparent in Figure 1: Returning to a pure toluene ambient restores the initial PL signal. Similar PL quenching is seen for CdS (458-nm excitation) from adsorption of C₆₀.

A dead-layer model can be used to quantitatively relate the PL quenching to the spatial extent of the electric field in the solid. Treatment of the near-surface region supporting the electric field as being nonemissive, because of its ability to separate electron-hole pairs, preventing their radiative recombination, leads to eq 1:

$$PL_{\text{ref}}/PL_{\text{flrn}} = \exp(-\alpha'\Delta D) \quad (1)$$

Here, PL_{ref} is the CdS(e) PL intensity in the toluene reference solvent; PL_{flrn} is the PL intensity in the presence of the fullerene; ΔD is the change in dead-layer thickness in passing from the toluene reference solvent to the toluene fullerene solution ($\Delta D = D_{\text{ref}} - D_{\text{flrn}}$); and $\alpha' = (\alpha + \beta)$ is the absorptivity of the solid for the exciting light, corrected for self-absorption.

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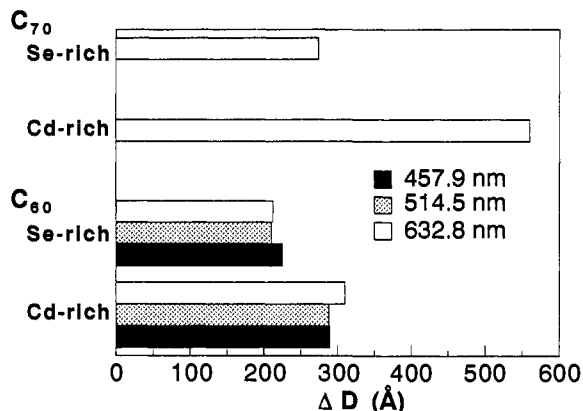


Figure 2. Maximum values of the expansion of the dead-layer thickness, ΔD , caused by the adsorption of fullerene molecules onto the Cd-rich (0001) or Se-rich (000 $\bar{1}$) face of an etched, single-crystal n-CdSe sample. Values of ΔD were calculated from PL quenching ratios by using eq 1 in the text. The concentration needed to produce these maximum changes in dead-layer thickness is $\sim 40 \mu\text{M}$. Excitation wavelengths used are indicated in the figure.

The data in Figure 1 were obtained with excitation wavelengths for which CdSe absorptivities span a factor of 3.¹⁰ The measured PL quenching ratios yield values for ΔD (eq 1), displayed in Figure 2, that range from $\sim 300 \text{ \AA}$ for C_{60} to over 500 \AA for C_{70} on the Cd-rich (0001) face (see below); substantial C_{70} solution absorbance at 458 and 514 nm precluded acquisition of meaningful ΔD values at these wavelengths. The consistent values obtained for ΔD with C_{60} with use of three interrogating wavelengths represent an excellent fit to the dead-layer model.

Quenching Dependence on Crystal Face. The CdS(e) samples employed in this study have the hexagonal wurtzite structure and therefore *c*-plates possess the two opposite polar faces shown in idealized form in Scheme I. Selective adsorption of anionic sulfurdonor species onto the Cd-rich (0001) face of CdS(e) has been reported.¹¹

The data in Figure 1 were obtained with the shiny (0001), Cd-rich face of CdSe. By simply turning the crystal around, the dull (000 $\bar{1}$), Se-rich face provides a second surface for investigation. We find that the fractional quenching is smaller on the Se-rich surface, but C_{70} still elicits greater quenching than C_{60} , although the difference between the fullerenes is more dramatic on the Cd-rich face. A good fit to the dead-layer model still obtains on the Se-rich face with C_{60} as the adsorbate, as shown in Figure 2; now, however, the expansion in ΔD is only $\sim 200 \text{ \AA}$ rather than $\sim 300 \text{ \AA}$ on the Cd-rich face. Similar behavior was observed with the strongly π -acidic TCNQ: The PL quenching was greater with the Cd-rich face of CdSe than with the Se-rich face.^{5a}

In interpreting these results it must be emphasized that Scheme I is an idealized picture: Given our experimental conditions, we cannot rule out the presence of another surface phase (an oxide, for example) or adsorbed species like oxygen and water. A possible explanation for why the Cd-rich (0001) face gives larger quenching with either fullerene than the Se-rich (000 $\bar{1}$) face may be that a greater number of adsorption sites are available when we use the (0001) face, leading to a greater effect on PL quenching.

Fullerene Acidity. As noted above, the fullerene-induced quenching of PL is consistent with the notion that these species are good Lewis acids. An idealized MO picture of the interaction is shown in Figure 3. Analogous to a weak charge-transfer complex in solution, we postulate that the LUMO of the fullerene is slightly destabilized and the distribution of surface states slightly stabilized (shifted toward the valence band edge) by adduct

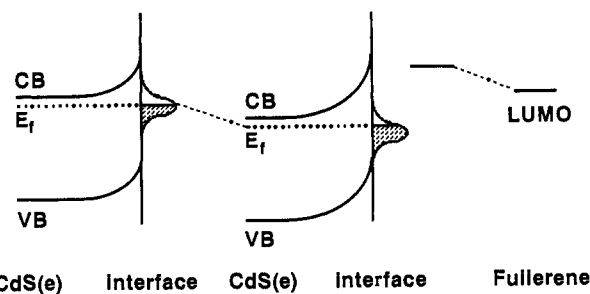


Figure 3. Perturbation of surface electronic states at the n-CdS(e) semiconductor surface by the lowest unoccupied molecular orbital (LUMO) of fullerene adsorbates. The interaction at the interface stabilizes the surface electronic states of n-CdS(e), moving them toward the valence band edge, and destabilizes the LUMO of fullerene adsorbates. Additional electrons move from the semiconductor bulk to fill the stabilized surface states up to the Fermi level, E_f , resulting in the expansion of the depletion layer (center part of the figure). The symbols CB and VB represent the conduction and valence band edges, respectively.



Figure 4. The initial PL spectrum of a n-CdSe single crystal [the Cd-rich (0001) face is exposed to the laser beam and solution] is presented at the left-hand edge of the figure: The remainder of the figure presents the PL intensity, monitored at the band maximum of 710 nm, as a function of the indicated C_{60} concentration in toluene solution. The sample is re-exposed to pure toluene at the end of the experiment. The exciting wavelength was 457.9 nm.

formation. Stabilization of the surface state distribution permits more electrons to be brought from the bulk to the surface, expanding the depletion width, which is reflected in our experiments as an expansion in the dead-layer thickness and a quenching of PL intensity.

At the longest excitation wavelength, 632.8 nm, the relative PL quenching of C_{60} and C_{70} can be directly compared. The greater quenching induced by C_{70} is intriguing. A three-dimensional Hückel molecular orbital (HMO) calculation done by Haddon et al. revealed that both C_{60} and C_{70} had low-lying LUMO's, with a slightly lower value of the LUMO energy level for C_{70} .¹² This calculation would predict that C_{70} is a better Lewis acid than C_{60} , although the reduction potentials of the two fullerenes have been virtually indistinguishable.^{2a} In terms of Figure 3, a lower energy LUMO for C_{70} would narrow the fullerene LUMO-surface state gap, stabilizing the surface state distribution to a greater extent than with C_{60} . The greater stabilization of surface states would bring additional electron density to the surface; and thereby enhance the ΔD expansion of C_{70} relative to C_{60} .

While our data are consistent with the notion that C_{70} is a better electron acceptor and more readily reducible, we do not know that the same coverage and binding sites are used when the two fullerenes adsorb. Therefore, no definitive statement can be made other than that the two molecules consistently produced these different quenching signatures.

Surface Adduct Formation Constants. The PL quenching by fullerene solutions is concentration dependent, as illustrated for C_{60} in Figure 4. Quenching of PL intensity can be detected at submicromolar concentrations of C_{60} , and the PL changes saturate at $\sim 40 \mu\text{M}$. We and others have found that the concentration

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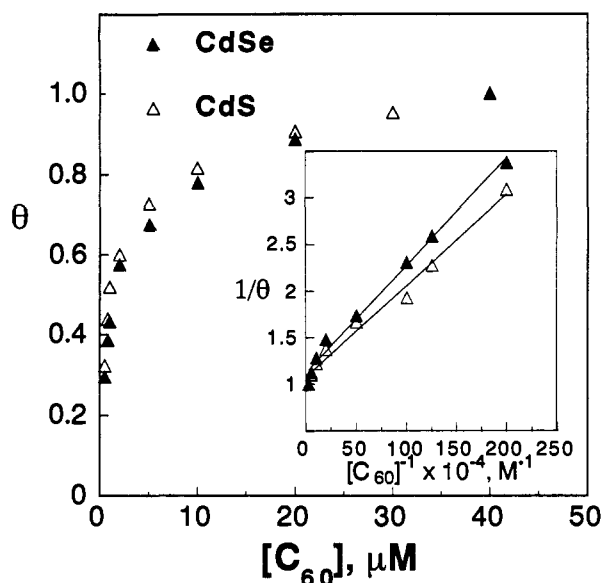


Figure 5. Plots of the fractional surface coverage, θ , defined in the text, as a function of C_{60} concentration for adsorption onto the (0001) face of CdSe (solid triangles) and CdS (open triangles). The linearity of the double-reciprocal plots (insets) implies a good fit to the Langmuir adsorption isotherm model. The binding constants, K , extracted from the double-reciprocal plots, are about 9×10^5 and 1×10^6 M^{-1} for the n-CdSe and n-CdS substrates, respectively. The excitation wavelength is 457.9 nm in both cases.

dependence of PL quenching can be utilized to estimate the equilibrium binding constant, K , using the Langmuir adsorption isotherm model.^{5,6,13} The quantitative form of the model is given in eq 2:¹⁴

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

where θ is the fractional surface coverage of the adsorbate, and C is the concentration of the adsorbing species in solution.

We assume that the adsorbate-induced PL changes are a measure of θ . Thus, for $\theta = 0$, the PL_{ref} value is used; for $\theta = 1$, the saturated PL intensity, PL_{sat} , is used; and for intermediate PL intensities, $\theta = \ln[PL/PL_{ref}]/\ln[PL_{sat}/PL_{ref}]$.^{6d}

Figure 5 presents PL quenching data as a function of C_{60} concentration for PL from the (0001) faces of CdS and CdSe; the inset of the figure shows double reciprocal plots using the same data. The adduct formation constant, K , can be extracted from the reciprocals of the slopes of the linear plots (eq 2). Large values for K of about 10^5 – 10^6 M^{-1} were obtained for toluene C_{60} solutions with both CdS and CdSe. The concentration-dependent PL quenching data for adsorption of C_{70} onto the (0001) face of CdSe is plotted in Figure 6. The binding constant of C_{70} is also in the range of 10^6 M^{-1} , similar to the value of K for binding C_{60} to the same surface. These equilibrium constants are among the largest we have measured with this technique and are comparable to those seen with another family of strong π -acids, derivatives of TCNQ.^{5a}

To confirm the comparable magnitude of equilibrium constants for the binding of C_{60} and C_{70} to the (0001), Cd-rich surface of n-CdSe, we conducted the competition experiment illustrated in Figure 7. Irrespective of whether C_{60} is added to a solution of C_{70} producing a saturated PL response or whether C_{70} is added to a solution of C_{60} producing a saturated PL response, the same intermediate PL intensity is observed upon exposure of the semiconductor to the same mixed ($C_{60} + C_{70}$) solution. This

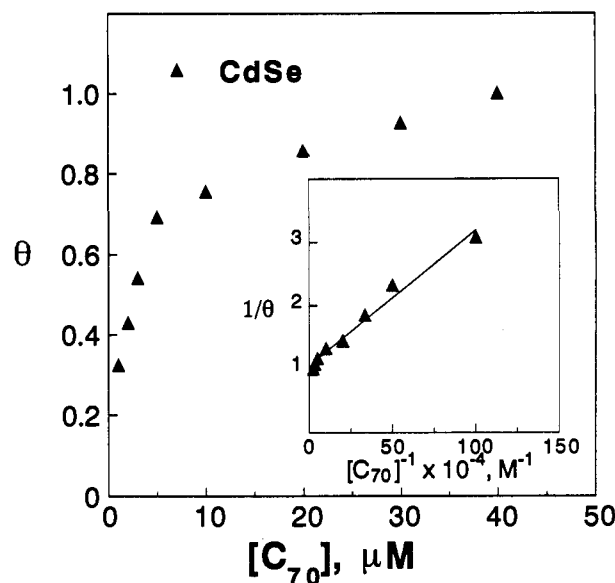


Figure 6. Plot of the fractional surface coverage, θ , defined in the text, as a function of C_{70} concentration. The data were obtained from the (0001) face of an etched, single-crystal n-CdSe sample. The linearity of the double-reciprocal plot of the data that is shown in the inset implies a good fit to the Langmuir adsorption isotherm model. The data shown correspond to an equilibrium binding constant K of 5×10^5 M^{-1} . The excitation wavelength is 632.8 nm.

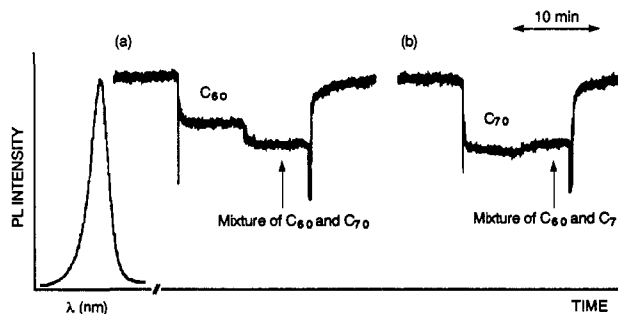


Figure 7. A competition experiment, based on fullerene-induced changes in the PL intensity (monitored at ~ 710 nm) of an etched, single-crystal n-CdSe sample [(0001) face]. The left-hand edge of the figure shows the initial PL spectrum obtained in pure toluene. Subsequently, (a) an 80 μM C_{60} toluene solution is injected into the sample cell, followed by addition of an equal volume of an 80 μM C_{70} solution, making the resulting solution 40 μM in both C_{60} and C_{70} . The experiment is then repeated (b) with the opposite order of addition: an 80 μM C_{70} toluene solution is injected into the sample cell, followed by addition of an equal volume of an 80 μM C_{60} solution, making the resulting mixed solution again 40 μM in both C_{60} and C_{70} . The excitation wavelength is 632.8 nm throughout the experiment. Downward spikes are from draining of solutions during the switching of liquids.

result demonstrates the lability of these adducts. Because the intermediate PL intensity of the mixed solution lies closer to the PL intensity of pure C_{70} solution, we believe that the surface in this experiment has a slight preference for C_{70} . It is interesting to note that the charge-transfer complex formed between C_{70} and N,N -diethylaniline (DEA) in methylcyclohexane solution is reported to have a slightly larger equilibrium constant than that found for the C_{60} /DEA charge-transfer complex.¹⁵

Dependence of Binding Constants on Crystal Face. As noted above, PL quenching is enhanced when a given fullerene is adsorbed onto the Cd-rich as opposed to the Se-rich face of CdSe. In contrast, use of the Se-rich face yields, within experimental error, the same binding constants for adsorption of either C_{60} or C_{70} as were found for the Cd-rich face. One possible explanation for these observations is that similar sites might be used on both faces by the fullerenes, but that there may be more such sites and

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associated states on the Cd-rich face: Note that, in the Langmuir adsorption isotherm model, the equilibrium constant for surface adduct formation is independent of the number of sites engaged in the equilibrium. Our data do not, of course, identify the sites used for binding or indicate why there would be more of them on the Cd-rich surfaces we have employed.

Conclusions

Bulk PL from CdS(e) can be a sensitive probe of surface adduct formation with fullerenes. In toluene solution, these species act as strong Lewis acids toward CdS(e), as evidenced by the substantial expansions in dead-layer thickness that they induce

and by their large binding constants for these surfaces. The C₆₀ and C₇₀ fullerenes can be adsorbed on both Cd-rich (0001) and Se-rich (000 $\bar{1}$) faces with binding constants on the order of 10⁵ to 10⁶ M⁻¹. Toluene solutions of C₇₀ consistently elicit greater quenching than do toluene solutions of C₆₀, although whether this reflects stronger intrinsic acidity or a difference in coverage and/or binding sites cannot be addressed by our data.

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