NMR studies of the surface structure and dynamics of semiconductor nanocrystals

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^{1}H NMR studies of thiophenol capping groups on cadmium sulfide nanocrystals demonstrate that the coverage of the capping molecule depends on the size of the nanocrystal. Data are presented which show that as the size of the nanocrystal increases, the coverage of thiophenol decreases. In addition, information about the overall tumbling of the nanocrystal and the motion of the capping groups relative to the surface can be obtained from linewidth studies, indicating that the rotation of the capping groups is hindered in the smaller nanocrystals ($r \approx 12$ Å) and becomes less so in larger nanocrystals ($r \approx 20$ Å). The coverage data are related to the electronic properties of this important class of compounds.

Cadmium sulfide nanocrystals have received much theoretical and experimental attention in the last ten years [1]. Intermediate between the molecular and the bulk, their electronic properties are size dependent [2], which raises the possibility of tuning these properties for technological purposes [3]. Not surprisingly, the surface structure of the particles plays an important role in determining many of the size-dependent properties. For example, trapping of the optically produced hole, the fluorescence of the nanocrystal, the surface energy and hence the phase diagram all depend upon the structure of the surface [4]. In addition, it is necessary to synthetically manipulate the nanocrystal surface to achieve solubility in a wide variety of organic solvents. Thus, a study of the organic molecules bound to the surface of the nanocrystal is crucial to our understanding of these systems. Despite its importance, however, the surface structure of these particles has so far received relatively little attention.

In this study we have used one- and two-dimensional solution state ^{1}H NMR to characterize the organic molecules bound to the surface of CdS nanocrystals. Despite the possibility of many different environments on the nanocrystal surface causing a featureless NMR spectrum, we have observed high-resolution, particle-size-dependent spectra. We show below how these studies can give us insight into the bonding arrangement of the organic molecules, their numbers and distribution on the surface, and their dynamics.

CdS nanocrystals capped with thiophenol were synthesized using inverse micelles according to standard procedures [5], except that they were not annealed and thus their interior was poorly crystalline. Four NMR samples of nanocrystals with different radii were prepared by dissolving 5 mg of CdS nanocrystals in 0.5 ml of 100% pyridine-d_5 into which a known amount of dry CH_2Cl_2 was added as an absolute intensity standard. 400 MHz ^{1}H NMR spectra were recorded within a week of particle synthesis at room temperature with Bruker AM-400 and AM-400X spectrometers. Two-dimensional phase-sensitive COSY spectra [6] were used to assign the chemical shifts. As shown in fig. 1 the aromatic region of the spectrum (covering a range from $\approx$6.8–8.8 ppm) displays several well-resolved resonances which allow us to conclude that the thiophenol is bound in

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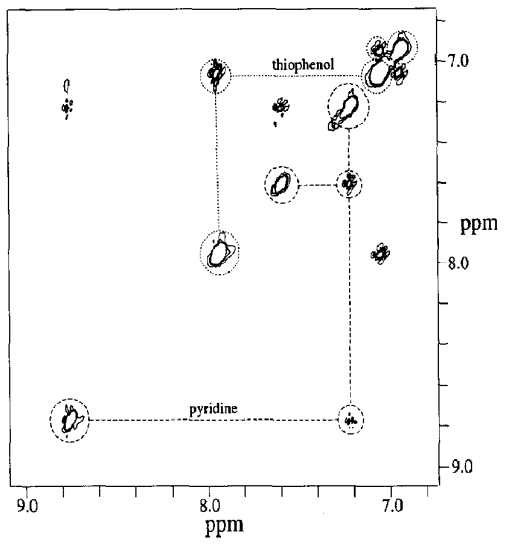

Fig. 1. Phase-sensitive ^{1}H COSY spectrum of the aromatic region of a sample of CdS nanocrystals capped with thiophenol. Note the characteristic connectivities shown for the ortho-, meta- and para-protons of the thiophenol. The spectrum was recorded using standard procedures on a Bruker AM-400 spectrometer.

discrete, well-defined sites on the surface, and indeed, when we study the two-dimensional COSY spectrum (fig. 1), we see only one set of resonances which are attributable to the ortho-, meta- and para-protons of thiophenol and which show the corresponding characteristic connectivities. Thus, the peaks at 7.91, 7.03 and 6.92 ppm are assigned to the ortho-, meta-, and para-protons respectively of thiophenol molecules bound to the surface. These peaks are substantially shifted from the free thiophenol resonances, but agree well with the solution state proton NMR spectra of model compounds, $Cd(SC_6H_5)_2$ and $[Cd(SC_6H_5)_2]_2[H_3CPCH_2CH_2PCH_3]$, both of whose crystal structures are known [7]. This result implies that thiophenol binds to cadmium atoms on the surface in a similar way in both the nanocrystal and the models. Unfortunately, we cannot use these data to specify whether thiophenol binds to the nanocrystal surface in a terminal or bridging manner, as the solution state structure of the models is unknown. The peaks at 8.71, 7.19 and 7.56 ppm are due to the ortho-, meta-, and para-protons respectively of residual protonated pyridine co-purified from the synthesis procedure. These resonances are identical to those in pure pyridine and disappear upon repeated evaporation and resuspension in deuterated solvent. Thus we may conclude that the pyridine is most probably associated with the nanocrystal surface and rapidly exchanges on and off the surface.

Using these spectra we are able to determine the number of thiophenol capping molecules per nanocrystal, and the percent coverage by comparing the integrated thiophenol signal to that of a standard present at known concentration (fig. 2 and table 1). The number of surface Cd atoms was determined for the thiophenol coverage calculation from the shell model of Lippens and Lannoo [10]. This model builds a nanocrystal by tetrahedrally binding atoms in shells starting from a single central atom and predicts the number of atoms N in a particle with a given number of shells n_s to be

$$N=\tfrac{1}{12}(10n_s^3-15n_s^2+26n_s-9) \quad \text{for odd } n_s\,, \tag{1a}$$

$$N=\tfrac{1}{12}(10n_s^3-15n_s^2+26n_s-12) \quad \text{for even } n_s\,. \tag{1b}$$

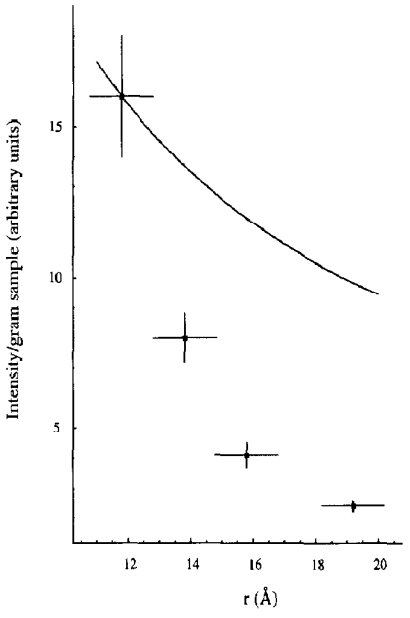

Fig. 2. Ratio of the number of para-thiophenol protons to the CH_2Cl_2 reference per gram of nanocrystal. The intensity falls in larger clusters, but not as the predicted $1/r$ dependence (solid line) predicted by simple surface to volume arguments; rather, assuming the approximate molecular weights given in table 1, the % coverage decreases in larger particles.

Table 1
Experimental measure of the coverage of thiophenol on CdS nanocrystals [a] as a function of nanocrystal radius [b]

Radius (Å) [b]	Molecular wt (kDa) [c]	Actual No. T.P./part	No. Cd on surface [d]	% Coverage of T.P.	Effective T.P. radius (Å) [e]	T_2 of T.P. para-peak (msec) [f]
11.8±1.0	23±6	24±6	92	26	9±1	57±3
13.8±1.0	34±7	18±4	162	11	12±2	76±3
15.8±1.0	50±10	16±5	204	7.8	14±2	121±3
19.2±1.0	89±14	17±5	304	5.6	16±2	220±3

[a] Determined by integration of the spectra presented in fig. 1.
[b] The radius of the nanocrystal, excluding the capping group using UV–VIS spectroscopy and graphs in ref. [8].
[c] Assuming the nanocrystal is spherical. This molecular weight is a lower limit.
[d] Based on ref. [8] and assuming completed shells. This coverage is a lower limit.
[e] Note that the Van der Waals radius of thiophenol is 2.1 Å if bound in a bridging fashion and is 4.9 Å if bound in a terminal fashion.
[f] T_2 was measured by the method of ref. [9].

This model is consistent with the nanocrystal preparation, which was performed with the addition of excess Cd at the end of the synthesis in order to create a Cd-rich surface. The nanocrystal radius is calculated assuming a spherical nanocrystal. Where the lattice constant of the unit cell is a, the radius is given by

$$r = \frac{a}{2}\sqrt[3]{\frac{3N}{4\pi}}. \qquad (2)$$

With these formulae, we can estimate an upper limit for the number of Cd atoms in the nanocrystal surface. The NMR data can then be used to provide a lower limit for the thiophenol coverage (table 1). *This percent coverage increases with decreasing nanocrystal radius.* The data show that the coverage increases from 5.6% to 26% as the nanocrystal radius change from 19.2 to 11.8 Å (table 1). Thus, the nanocrystal is not completely capped. It is of considerable interest to determine whether the thiophenol molecules are uniformly dispersed at low coverage on the nanocrystal surface, or if there are substantial local fluctuations in the coverage. If the thiophenol coverage were uniform, the average distance from one surface molecule to another would change from 18 to 32 Å. Such large separations would indicate that there should be negligible interaction between thiophenol molecules.

Perhaps the most remarkable feature of fig. 3 is the size dependence of the linewidths of the thiophenol peaks. As the nanocrystals become smaller, the resonances broaden. This broadening could be either homogeneous as a result of changes in the mechanism of motional narrowing of the lines, or inhomogeneous and due to site variations on the nano-

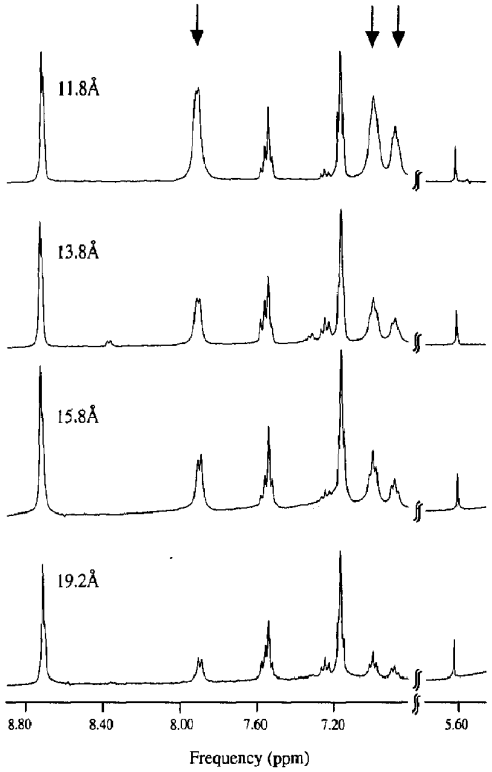

Fig. 3. ^{1}H NMR spectra of solutions of cadmium sulfide nanocrystals. For each spectrum the core radius of the nanocrystal is (a) 11.8, (b) 13.8, (c) 15.8 and (d) 19.2 Å. The arrows indicate the thiophenol resonances and the peak at 5.68 ppm corresponds to the calibrated intensity reference of CH_2Cl_2.

crystal surface. Selective transverse relaxation time (T_2) measurements demonstrate that this broadening is homogeneous. Fig. 4 shows the selective T_2 pulse sequence of Emsley, Kowalewski and Bodenhausen [9] that was used to make the measurements, together with some representative T_2 data. The resulting transverse relaxation times (given for the para-peak in table 1) fully account for the trend in the linewidth, demonstrating that the lines are in fact homogeneously broadened. Therefore, the changes in linewidth must be due to motional averaging effects. There are three types of motion that can effect the relaxation of the thiophenol protons: (i) isotropic tumbling of the entire nanocrystal, (ii) motion of the thiophenol with respect to the nanocrystal surface, and (iii) motion of two surface bound thiophenol molecules with respect to each other. Isotropic tumbling of the entire nanocrystal assumes that the thiophenol ligands remain fixed with respect to the nanocrystal surface and the whole particle undergoes isotropic rotational diffusion as described by the Stokes–Einstein equation. This predicts that as the particle size increases from 11.8 to 19.2 Å, the isotropic correlation time increases from 1.7 to 7.1 ns, and that the transverse relaxation time should correspondingly decrease with increasing nanocrystal radius. Also, if only intra-thiophenol dipole–dipole interactions are considered, the ratio of T_2^{para} to T_2^{ortho} should be 0.5. Neither of these predictions is borne out in our experiment data, presented in fig. 5.

As a first step towards improvement of our model, we added reorientation of the thiophenol molecules with respect to the nanocrystal surface and included only intra-thiophenol dipole–dipole interactions. We calculated the relaxation behaviour for bridging thiophenol molecules, where the only rotational degree of freedom is about the S–C bond, and for those molecules bound terminally, where the thiophenol molecule can rotate about both the Cd–S and S–C bonds. These models both predict that the transverse relaxation times should increase as the bond rotation rates increase. This result is in agreement with intuition, since at 400 MHz the isotropic tumbling of the entire nanocrystal is in the slow motion regime and bond rotations can only serve to decrease the effective dipolar coupling between neighbouring protons and thus increase the transverse relaxation times.

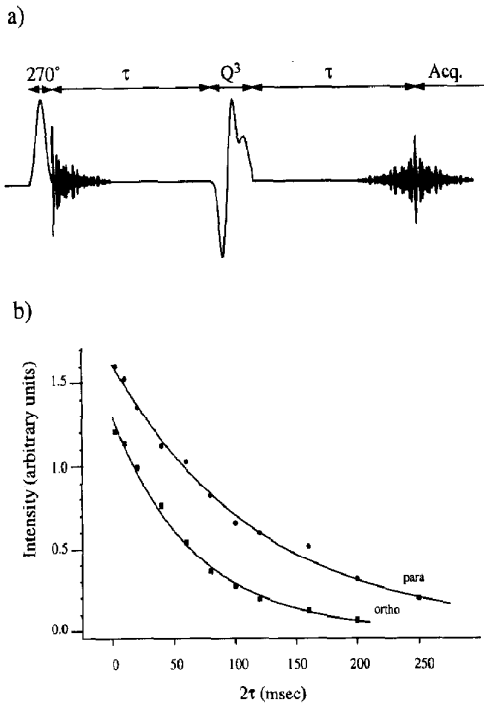

Fig. 4. (a) The selective T_2 pulse sequence of Emsley, Kowalewski, and Bodenhausen [9] used to measure the tranverse relaxation times of the thiophenol protons on the nanocrystal surface. The first 270° Gaussian pulse excites magnetization of a single multiplet, the magnetization then dephases during a time τ at which point the Q^3 inversion pulse is applied to refocus the magnetization after a second τ period which is followed by acquisition of a free induction decay. (b) Ortho- and para-T_2 data obtained using the sequence of (a) for the 15.8 Å radius nanocrystals.

The insert in fig. 5 shows an example of the calculation of the ratio of T_2^{para} to T_2^{ortho} for a terminally bound thiophenol molecule undergoing rotational diffusion about both the Cd–S and S–C bonds. The correlation time for tumbling of the entire nanocrystal was set at 10 ns and the two bond rotation rates were varied from 0.1×10^{11} to 10×10^{11} s^{-1}, which corresponds to varying the correlation times from 1 to 100 ps. As can be seen from the insert, only very slow rotation rates can predict the observed ratio of T_2^{para} to T_2^{ortho}, which varied from 1.24 to 2.18. Unfortunately, these slow rotation rates do not correctly predict the absolute magnitude of the ortho-T_2. In addition, the rates necessary for such ratios correspond to correlation times longer than 100 ps, which are unrealistic because they would require un-

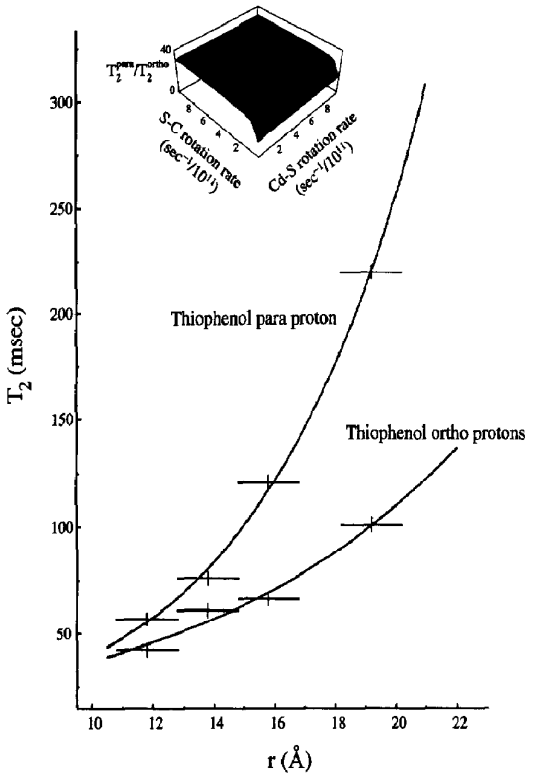

Fig. 5. T_2 of ortho- and para-protons versus size. The solid lines represent a fit of $a_1 \exp(a_2 r)$ to the data. Inset we show that the ratio T_2^{para}/T_2^{ortho} calculated assuming purely intra- molecular contributions to relaxation as a function of the rotation rate (defined as $1/\tau_c$) about the S–C and S–Cd bonds. Note how this ratio is always much larger than any of the experimentally observed ratios.

reasonably high barriers to rotation. (Even in the densely packed interiors of proteins, where strong steric interactions should quench rotational motions, aromatic rings are known to undergo 180° hops with correlation times in the picosecond range.) Thus, this model could not realistically predict our data. Note that the results do not change significantly when we consider either bridging or terminally bound thiophenol molecules, or when we use a model based on discrete hops in either the strong or weak limit instead of rotational diffusion.

Since the motion of a single thiophenol molecule with respect to the nanocrystal surface is insufficient to describe our data, an inter-thiophenol relaxation mechanism was included in the model. In order for the ratio of T_2^{para} to T_2^{ortho} to be depressed, inter-thiophenol relaxation must primarily affect the para-relaxation. It is only possible for the inter-thiophenol relaxation to be comparable to the intra-thiophenol contribution if para-protons on different thiophenols can closely approach one another, which implies that the thiophenol molecules must be terminally bound to the surface. Given the r^{-6} dependence of dipole–dipole relaxation, our models show that such an inter-molecular effect can only significantly depress the ratio of T_2^{para} to T_2^{ortho} if the distance of closest approach between para-protons is about 1 Å. The para-protons can come this close to one another if the distance between binding sites is about 10 Å. If we include this inter-molecular contribution we are able to reproduce our data by assuming a correlation time for internal motion about the S–Cd and S–C bonds of ≈ 20 ps (which would appear typical for this type of motion) which varies slightly with particle size, getting shorter as the particle gets larger. This is consistent with the steric effects implied by the observed decrease in thiophenol coverage on larger particles. The calculated ratio of T_2^{para} to T_2^{ortho}, under these restraints, agrees well with experiment. (The meta-protons have not yet been considered in this discussion because of the mathematical difficulty in describing the motion responsible for their intermolecular relaxation.) Note that these measurements provide essentially independent determinations of the inter- and intra-molecular contributions to relaxation. The absolute value of the ortho-proton relaxation rates are governed purely by intra-molecular effects whilst the ratio between the ortho- and para-rates is largely governed by inter-molecular effects. If the distance between thiophenol molecules determined from the relaxation data is compared to twice the thiophenol radii calculated by assuming a homogeneous thiophenol distribution as presented in table 1, we can only conclude that the thiophenol molecules must congregate on the surface to form islands of covered regions with the density of coverage in these islands decreasing slightly as the nanocrystals get larger.

In conclusion, we have presented the first NMR study of the surface structure of semiconductor nanocrystals. It seems that these spectra, while at first sight appearing relatively simple, conceal a wealth of information about the nature of the surface. The spectra show that the nanocrystal surface is not com-

pletely capped. Rather, due to nanocrystal faceting, steric effects or kinetic limitations of the capping process, islands of covered regions exist which are separated by uncovered regions. Furthermore, our model of inter- and intra-molecular proton transverse relaxation is able to describe the absolute magnitude, as well as the ratio, of the ortho- and para-T_2 and has begun to provide insight into the striking size dependence of the T_2. The thiophenol T_2 are dependent on both the rotation rates and the average number of neighbouring thiophenol molecules. Clearly changes in these parameters as a function of the nanocrystal radius should explain the size-dependent T_2 and will allow NMR measurements to provide more information on the distribution of thiophenol molecules on the surface as well as the intermolecular potential determining the thiophenol rotation rates. Although our results are only preliminary, our data strongly indicate that the capping thiophenol molecules are terminally bound to the surface. We are currently extracting this information from our data, which we intend to complement with the results of ^{13}C relaxation studies.

Until now, such detailed information about the structure and dynamics of surface capping molecules on nanocrystal surfaces has been difficult to obtain. NMR appears to be an ideal tool for extracting this information, which is needed in order to understand fully such properties of the nanocrystal as ultrafast trapping of photon-generated electrons and holes [11]. By binding organic molecules to the surface, one hopes to move all mid or near band gap surface states to much higher energies. Clearly, to accomplish this, the coverage will need to be increased to saturation. A more detailed interpretation of these results in terms of their impact on nanocrystal properties, together with the results and details of the relaxation studies will be presented elsewhere [12].

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