Electronic Supplementary Information

For

Interaction of Substituted Poly(phenyleneethynylene)s with Ligand-Stabilized CdS Nanoparticles

by

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S1. Surface Chemistry of Ligand-Stabilized CdS Nanoparticles

Details of the synthesis of ligand-stabilized nanoparticles and their surface chemistry have been investigated by elemental analysis, XPS, NMR, EXAFS, IR, and UV/Vis spectroscopy.[S1-S10] Consistent with these data, it is likely that the synthesis of CdS from $CdSO_4$ and $(NH_4)_2S$ in the presence of MPS thiol (R-SH) first leads to the formation of CdS (eq (S1)), and in a second step to the replacement of superficial sulfide by the thiol ligand R-SH (eq (S2)):

$$CdSO_4 + (NH_4)_2S \longrightarrow CdS + (NH_4)_2SO_4 \qquad (S1)$$

$$(Cd_nS_n)_{core}(Cd_mS_m)_{outer\ layer} + 2p\ HS\text{-}R \longrightarrow (Cd_nS_n)_{core}[Cd_mS_{m-p}(S\text{-}R)_{2p}] + H_2S \qquad (S2)$$

This sequence of reaction steps is likely because the free energy of CdS formation (eq S1) is lower than for the alternative formation of $Cd(SR)_2$ that would produce sulfuric acid:

$$CdSO_4 + 2\ HS\text{-}R \rightleftharpoons Cd(SR)_2 + H_2SO_4 \qquad (S3)$$

If the reaction in eq (S3) were to occur, $Cd(SR)_2$ would then react back to $CdSO_4$ and release the weaker acid R-SH. Therefore, once CdS is formed according to eq (S1), the substitution of superficial sulfide by the thiol according to the suggested mechanism is more likely (eq (S2)). The reaction then involves atoms on the surface of the nanoparticle and the production of a small amount of H_2S (a weak acid). Thereby, every pair of incoming thiol molecules would replace one sulfide ion and require one additional coordination site on the surface, which could be provided by superficial cadmium ions (eq (S2)).

In this suggested process, the actual number of groups on the surface increases upon ligand binding from m sulfide groups to a mixture of (m-p) sulfide groups and ($2p$) thiol groups. The total number of groups on the surface could hypothetically double the number of original sulfide ions to ($2m$) thiolate ions. To which extent the reaction proceeds is somewhat uncertain due to incomplete experimental evidence. It may be possible that only a few ligands are attached, such as 1 thiol group per nm^2 (p~$0.1m$).[S1, S10] The stoichiometric maximum of thiol coverage as twice the number of initial sulfide ions is not possible because steric reasons set a limit at about half this amount ($p \leq 0.5m$). The reason is that the maximum area density of single alkyl chains cannot exceed approximately 5 per nm^2 due to a cross-sectional area of 0.188 nm^2 for an all-anti configured alkyl chain. Therefore, at most, about half the sulfide ions could be exchanged ($p=0.5m$). The maximum surface coverage with sulfur species would then involve one third sulfide groups ($m/2$) and two thirds thiol groups (m) if this mechanism is true.

Due to some remaining uncertainty about the mechanism of formation, surface chemistry, and exact coverage with thiols, two simplifying assumptions are made in the models. First, coverage with thiols near maximum is assumed, i.e., 4.5 per nm^2 and $p=0.5m$.[S1, S10] Second, all thiol ligands assume the location of the m superficial sulfide ions, and the presence of additional $m/2$ sulfide ions is neglected (the corresponding negative charge is equally distributed over the thiol sulfur atoms to maintain charge neutrality). Even though this arrangement is non-stoichiometric, arbitrary assumptions of how to distribute sulfide and thiolate ions on the surface are avoided.

Therefore, this study is limited to the introduction of the very first models and their application. Follow-on simulation studies of various surface chemistries with correct stoichiometry and ionic distributions of ligand-stabilized quantum dots will be valuable, especially when coordinated with measurements, to provide new insight and guidance in atomic-scale design.

S2. Details of the Force Field for CdS and Validation

S2.1. Energy Expression and Balance of Ionic Versus Covalent Bonding. The PCFF force field was chosen to facilitate applicability of the CdS parameters for interfaces with organic compounds and solvents following the INTERFACE approach (Tale S1).[S11] The relevant portion of the PCFF energy expression for cadmium sulfide consists of Coulomb and Lennard-Jones terms for nonbonded interactions (electrostatic and van-der Waals contributions):

$$E_{pot} = \frac{1}{4\pi\varepsilon_0} \sum_{\substack{ij\ nonbonded \\ (1,3\ excl)}} \frac{q_i q_j}{r_{ij}} + \sum_{\substack{ij\ nonbonded \\ (1,3\ excl)}} \varepsilon_{ij} \left[2\left(\frac{\sigma_{ij}}{r_{ij}}\right)^9 - 3\left(\frac{\sigma_{ij}}{r_{ij}}\right)^6 \right] \tag{S3}$$

These terms offer a suitable description of minerals, as previously shown.[S11-S14] The application of standard combination rules enables the simulation of interfaces with solvents, organic, and inorganic molecules. For cadmium sulfide, bonded terms for bond stretching, angle bending, torsions, and out-of-plane vibrations are not absolutely necessary because the mineral is only about half covalent with atomic charges of +1.0e for Cd^{2+} and -1.0e for S^{2-} (±0.1e). The semi-ionic character with about 50% ionic contributions to bonding is reflected by the nearest neighbor Cd ··· S distance of 2.52 Å that exceeds typical bond lengths. The situation is similar for

ZnS that is known to be both ionic and covalent.[S15, S16] The addition of terms for bond stretching and angle bending could still have merit to better approximate covalent contributions to bonding and lower thermal fluctuations of the atoms in their lattice positions. However, a minimum number of parameters was chosen here for an initial, structurally stable model (Table S2).

S2.2. Interpretation of Parameters. Since bonded terms are excluded, the interpretation of Lennard-Jones (LJ) parameters differs somewhat from minerals with stronger covalent character such as silicates and many aluminates.[S11, S13, S14] While in such minerals, σ_{ii} more closely reflects atomic diameters, in the CdS model, σ_{ii} is closer to ionic diameters and chosen to match the ratio between cation and anion size <0.414 that is necessary to stabilize 4:4 coordination.[S16] The role of ε_{ii} also reflects less the atomic polarizability and the number of nonbonded neighbors under consideration of exclusions (e.g. 1,4 bonded atoms) that dominate in covalent environments, but ε_{ii} rather contributes to the strength of repulsion needed to counterbalance Coulomb attraction. Thereby, a higher value of ε_{ii} (steeper repulsion at short distance) is equivalent to a higher value of σ_{ii} (repulsion at larger distance), and a smaller value of ε_{ii} is equivalent to a smaller value of σ_{ii}. For example, σ_{ii} = 480 pm and ε_{ii} = 0.40 kcal/mol for sulfide ions, as chosen, is very similar to the alternative choice σ_{ii} = 570 pm and ε_{ii} = 0.04 kcal/mol, where the ε_{ii} value equals that of the cadmium ions. The first choice is more realistic, however, due to more proximity to true ionic size and expected higher polarizability.

S2.3. Validation and Opportunities. All atoms are flexible in the model. Nearest neighbor distances and angles are reproduced with less than 0.5% deviation from X-ray data.[S17, S18] Cell parameters and density agree near perfectly with experiment (<0.1% deviation), and the model is thermally stable up to at least 700 °C.

Further validation of surface and interfacial properties (cleavage energy, hydration energy), as well as mechanical properties, may lead to refinements of this model in future work. Extensions to other force fields with 12-6 Lennard-Jones potentials, such as CHARMM,[S19] AMBER,[S20, S21] CVFF,[S22] and OPLS-AA[S23] are possible by transcription of the parameters σ_{ii} and ε_{ii} with known adjustments.[S11, S13, S14, S24] Similar force field settings, potentially extended with covalent terms, can be applied to an entire group of quantum dots such as (Zn, Cd)(S, Se, Te).

Table S1. Force field parameters for β-CdS (Hawleyite) within the PCFF energy expression (eq (S3)).

Atom type	$q_i\,(e)$	σ_{ii} (pm)	ε_{ii} (kcal/mol)
Cd^{2+}	+1.0	215	0.04
S^{2-}	-1.0	480	0.40

Table S2. Cell parameters of β-CdS (Hawleyite) according to X-ray data (ref. [S17, S18]) and molecular dynamics simulation in the NPT ensemble under standard temperature and pressure.

Method	Cell dim.	a (nm)	b (nm)	c (nm)	α (°)	β (°)	γ (°)	ρ (kg/m^3)
Experiment	4×4×4	2.3328	2.3328	2.3328	90	90	90	4838 (10)
PCFF	4×4×4	2.3330	2.3330	2.3330	90	90	90	4838 (20)

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