Electronic Structure of CDs Nanoparticles Modified at the Chalcogen Sites and Luminescence Effects

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ABSTRACT

In this work we report a theoretical study on the use of surface modifiers of CdS nanoparticles (NPs) consisting of incompletely coordinated asymmetric metal complexes with labile and strong ligands. The sulfur centers on the NP surface replace the weak labile ligands, while the strong organic ligands in the complex provide adequate molecular orbitals for the interaction with the NP. The metal complex used in this study (previously synthesized by this group) is aqua(2,2'-bipyridyl-N,N')(malonato-O,O')-copper(II) monohydrate, (CuBM). To help understand the optical changes in the modified NPs, a density functional theoretical study (DFT) of the NP surface was carried out at the DFT p-BP86/DN(*)//PM3 level of theory. The modified NPs are modeled by an elementary cell of cubic CdS with attached CuBM unit. One of the S atoms in the cube is bound to the Cu center in the CuBM moiety. The dangling bonds of sulfur atoms of the cluster representing the interface with atoms of the crystal lattice inside the NP were passivated with CH 3 groups. The calculated molecular orbitals for this model cluster describe the new surface states of the CuBM-modified NP.

Keywords: Theoretical, Nanoparticles, Semiconductor, CdS, Surface Modification

1. INTRODUCTION

II-VI semiconductor nanoparticles (NPs), such as cadmium chalcogenides, represent a new type of chromophores for which adsorption and emission bands are controlled by the diameter of the particle. [1] Surface modification has been shown to optimize the intrinsic optical properties of nanomaterials producing highly luminescent colloids [2] with a variety of applications. [3 - 4] At the same time, surface ligands with chemical specificity can introduce a higher level of NP structural organization and new chemical/optical properties. In many studies on the surface modification of II-VI semiconductor NPs with different organic ligands, their pairing with optically active compounds such as dyes, aromatic hydrocarbons, etc., was aimed at finding the effects from the charge carrier exchange between the electronic levels of a NP core and a modifier. [5]

Evidence of NP-NP and NP-modifier carrier exchange shows up as conductivity changes when interparticle bridges replace partially the stabilizer layer and stimulate such processes via conjugation through aromatic heterocycles [6 - 7] or aromatic thiols. [8 - 10] All current strategies of II-VI semiconductor NP functionalization are based either on the exchange of a stabilizer bound to the metal sites on the NP’s surface or on the chemical modification of its terminal group. However, there is a substantial energy mismatch between the surface Cd ions and the conduction band of the semiconductor NPs, which creates an energetic hurdle for the effective interaction between the carrier levels. [11] In the other hand, this barrier is much lower for corresponding S sites because, unlike metal sites, the energy states of surface S atoms are partially mixed with the valence band of CdS. [11] This low barrier makes them suitable for the preparation of conjugated electronic systems.

We have recently reported a new synthetic approach to utilize S sites of CdS for surface modification and demonstrated the formation of novel supramolecular structures made of NP and transition metal complexes. In the present work, we report a theoretical study and analysis of our previously synthesized and modified NPs as well as
the electronic processes involved and modification of the optical properties. Such systems would be of great interest for many applications of NPs including molecular electronics, catalysis, and NP lasing [3-13-14]. The fact that both NP and metal complexes are versatile chromophores, can produce a large new class of supramolecular compounds, for which the quantum effects of NPs are combined with optical properties of transition metal complexes.

2. EXPERIMENTAL METHODOLOGY AND RESULTS [12]

The chalcogen centers on the NP surface are to replace the complex weak labile ligands, while the strong organic ligands will provide adequate molecular orbitals for the interaction with NP. The reaction of surface modification is schematically depicted in Figure 1. The metal complex used in this study is aqua(2,2'-bipyridyl-\(N,N'\))(malonato-\(O,O'\))-copper(II) monohydrate (CuBM) [15] (Figure 1). The choice of this modifier was made on the basis of the strength of the Cu-S bonding and the spectral characteristics of CuBM, that are quite distinct and do not overlap with the band edge of the NPs, where spectral changes caused by the modification may occur.

![Figure 1](image)

Figure 1. Schematics of our chalcogen modification of II-VI semiconductor NPs with mixed ligand transition metal complexes.

Experimentally it was noted [12] that the increase of Cd\(^{2+}\) concentration results in the reduction of particle size, which can be understood as the result of the increase of NP surface charge and related to the electrostatic adsorption of the citrate stabilizer employed. The particle diameter can be varied from ca. 26 to 44 Å, which is sufficient for the observation of size effects in the modified species. The emission properties are dominated by the trapped emission luminescence with maximum shifting from 620 to 670 nm as NP diameter increases. The excitonic emission is weak, as is common for uncoated CdS NPs. Nevertheless, it is still easily recognizable in the peak in the blue part of the spectrum, which varies between 425 and 455 nm for the available particle diameters. The observed quantum yield of the trapped and excitonic emission bands is 6.0-7.5% and 0.15-0.15%, respectively.

The reaction of CdS and CuBM does not change the diameter of the NP’s cores remaining at 3.3 nm. One could
expect substantial modification of the luminescence pattern of NPs upon the attachment of CuBM. Indeed, the emission spectra are found to be quite different from those for parent NPs, and they also depended on the region where the product is excited. For 290 nm excitation wavelength, we see the appearance of a new band at 360 nm for CuBM-modified NPs. For 340 nm excitation light, a new band at 445-450 nm is observed. Simultaneously, a decrease of intensity and red spectral shift of the trapped emission of NPs at 600-700 nm occur. The new luminescence bands at 445-450 nm and 600-700 nm do not depend on particle size. A very strong new peak appears at 300 nm after the attachment of CuBM to CdS, while the features in the 350-500 nm region coincide with those of naked NPs.

All the experimental procedures related to the synthesis, characterization and modification of the NPs are described in detail in our previous paper [12].

3. THEORETICAL AND COMPUTATIONAL METHODOLOGY AND RESULTS

Because of the thousands of atoms occurring at the NPs of the experimentally studied sizes [12], (between 26 and 44 Å in diameter), the computational cost of electronic structure calculations is prohibitive even with state-of-the-art hardware and software. Therefore, our previous successfully employed cluster model [16] is used to simulate the NP-modifier system. Once the cube model cluster was set for the NP-modifier system, we initially obtained a Semiempirical [17-18] PM3 optimized geometry. The obtained geometry was tested to correspond to a global potential minimum through analysis of the resulting Hessian frequencies. Keeping this geometry, we thereafter obtained single point energy, wave function, and orbitals at a higher level of theory,[17] performing a density functional calculation[19] with the exchange functional of Becke[20] and the correlation functional of Perdew (BP86) which provides reliable results for both occupied and unoccupied states[21]. The DN(*) numerical basis set, similar in size to the 6-31G(d) Gaussian basis set[22], was used. Furthermore, post SCF gradient corrections are included on a perturbative manner. Therefore, the achieved level of calculation is denoted as p-BP86/DN(*)//PM3. For all calculations and visualizations, the Gaussian 94[23] and Spartan V5.1 software packages were employed.[22]

The modified NPs simulated by an elementary cell of cubic CdS (in accord with X-ray diffraction data with attached CuBM unit) are presented in Figure 2a. The model consists of four Cd and four S atoms with one of the S atoms in the cube being bound to the Cu center in the CuBM moiety. The calculated molecular orbitals for this model cluster approximate the new surface states of the CuBM-modified NP. The dangling bonds of sulfur atoms on the left side of the cluster representing the interface with atoms of the crystal lattice inside the NP were saturated with CH₃ groups. These end-groups were chosen instead of simpler hydrogen capping to avoid artificial intramolecular hydrogen bonding which would distort both the geometry and the electronic orbitals of the cluster. The occupied and empty electronic states are denoted here as HOMOs and LUMOs, respectively, with HOMO 1 and LUMO 1 being the frontier orbitals. Among the molecular orbitals calculated, there are electronic states enveloping atoms of both the NP surface and the modifier exemplified by LUMO 1 and HOMO 1(Figure 2b,c). HOMO 6 (Figure 2h), HOMO 7, HOMO 8, and LUMO 10 (not shown). The distribution of electron density in the orbitals reflects the involvement of different parts of the complex and the surface of the NP. It was noted that LUMOs tend to concentrate predominantly on the aromatic bipy part of the CuBM moiety, while HOMOs are more often localized on the CdS part. The sequence of the LUMOs and HOMOs provides insight into the photophysics of the modified NPs revealing possible excitation relaxation pathways of electrons and holes, respectively, in accordance to the luminescence data.
4. DISCUSSION

4.1 Structure of the Chalcogen-Modified CdS Nanoparticles.

Before the discussion of the optical properties of CuBM modified CdS NPs, some structural information about the product of the reaction in Figure 1 needs to be established. The ESR spectra [12] unequivocally demonstrate the reduction of the copper metal center of CuBM. The disappearance of the ESR signal indicates the transition from the paramagnetic 3d9 state of Cu(2+) to the ESR-invisible diamagnetic 3d10 state Cu(1+). Such a reaction is typical for binding of Cu(2+) to various thiols and other sulfur-containing groups [24-26] including CdS NPs [25].

The reduction of Cu(2+) complexes by thiols and similar species always leads to Cu-S covalent bonding. The formation of the Cu-S bond is accompanied by restructuring of the coordination sphere of the metal and replacement of the weaker/harder ligands because of the high affinity of these atoms to each other characterized as soft Lewis acids and soft Lewis bases. Considering that there are approximately 120 surface atoms of sulfur in tetrahedral 34 Å CdS NP, the decoration with CuBM is rather selective because of:

1. Differences in nucleophilic character of different sulfur atoms on the NP surface in different atomic environments and
2. The spatial constraints for accommodating the bulky metal complex units.

Figure 2. Molecular orbitals of CdS-CuBM model cluster computed at the p-BP86/DN(*)//PM3 level of theory. In (a) the CuBM-NP basic unit is shown. All others are different molecular orbitals.
Therefore, the structure of the product of the modification reaction in Figure 1 can be described as a few tens (<40) of CuBM units attached via a Cu-S bond to the surface of NPs. The total number of the decorating metal complex molecules may, of course, vary depending on the amount of CuBM added and the diameter of the NP. In perspective, the reduction of the overall number of the metal complex units bound to the NP may be desirable for the synthesis of multiparticle associates, while the increase of the modifier density will be beneficial, for instance, in catalysis.

4.2 Surface Electronic Structure.

Different molecular orbitals corresponding to this model cluster, see Figure 2a, unveil how the surface of CdS NP and the transition metal complex modifier interact in the prepared supramolecules. What seems to be an important and novel feature of the electronic structure is the formation of delocalized unoccupied and occupied molecular orbitals enveloping the surface atoms of CdS, copper atom, the organic ligands of the transition metal complex, such as LUMO 1, HOMO 1, HOMO 6, and others (Figure 2b,c,h). Apparently, the delocalized molecular orbitals are characteristic for the chalcogen modification of NPs with metal complexes because similar calculations done for cubic CdS cluster with thiophenyl moiety attached to one of the Cd atoms (Figure 3-1) did not reveal any hint of bridging orbitals involving the π-system of the phenyl ring. Such orbitals are also not seen for a bigger model Cd_{10}S_{4}(SPh)_{16}^{4-} that closely resembles small NPs with large number of aromatic phenyl rings (Figure 3-2). It is clear that no d-orbitals of Cd atoms are involved in the formation of the corresponding HOMOs or LUMOs, as was expected from the fact that they are fully occupied. The difference in molecular orbitals obtained for chalcogen and metal anchoring of aromatic molecules originates in the availability and overlap difference of the atomic orbitals forming the link between the NP and the modifier.

In the CdS/CuBM supramolecule, the sulfur sites are capable of p-bonding via available p-atomic orbital carrying one electron on it after partial oxidation by Cu(2+). These p-orbitals overlap with a butterfly d-orbital of copper (Figure 2b,c,f). This can be observed for the frontier molecular orbitals HOMO 1 and LUMO 1 as well as for other molecular orbitals such as HOMO 2 (Figure 2b,c,f). At the same time, the butterfly d-orbital overlaps with the p-orbitals of nitrogen forming the aromatic system of bipyridine and oxygen atoms of the malonic acid in the fashion presented in Figure 3-3. Thus, the d-orbitals of the transition metal realize the bridging between the p-orbitals of sulfur on the surface of NP and the π-system of the aromatic ligands of the complex such as bipyridine. Moreover, the S-Cu-N atomic sequence is quite effective for the conjugation of the NP surface with organic aromatic systems because both parts are linked by one atomic orbital of the transition metal with very convenient symmetry and orientation for that purpose. Such a mode of bridging is certainly not available for Cd-S-C or Cd-N-C atomic groups present in NPs modified via Cd-atoms, because the middle atom has to engage orthogonal p-orbitals for the interaction with both parts of the system. Moreover, the mixing of p-orbitals of S and N with the butterfly d-orbitals of transition metal (Figure 3-3) diminishes the disparity in their energy levels.
4.3 Luminescence Properties.

These properties strongly depend on the surface processes, and there is a dramatic change in the emission pattern, which bears little resemblance with any modified NPs studied previously. There are two new emission bands at 350 and 414 nm, while the broad band of the red luminescence at 600-700 nm shifts to 630-750 nm.

(1) Short lifetimes of the new emission bands at 350 and 447 nm indicate that they are not regular d-d emissive transitions of copper ions, that are known to be forbidden and have lifetimes >10 s.[27]

(2) The 447 nm peak is not an enhanced excitonic band of the NPs, although it is located in the same spectral region, and its lifetime coincides with those previously reported for excitonic electron/hole recombination.[28] The reason for this conclusion is the fact that the position of the new band does not depend on the particle size, which should be expected for the CdS excitonic emission.

(3) Because we are interested in the effects occurring on the NP surface, the major focus of the discussion will be placed on the luminescence of NPs at 600-700 nm. This band is typically attributed to the emission of the charge carriers trapped in the surface states undergoing the recombination between themselves and/or with the carriers on the conduction and valence bands.

What is quite peculiar about this luminescence is that its lifetime increased from 64-78 to 110-115 ns after reaction with CuBM, while the overall intensity decreases. This contradicts the common scheme of dynamic luminescence quenching of NPs when both intensity and the lifetime decrease due to more intense nonradiative processes.[29] This observation also has no analogies in data obtained for other NP-dye assemblies reported so far; the lifetime of NP red emission inevitably decreased as a result of electron and/or Förster energy transfer quenching.[30]

We believe that the explanation for the effect of lifetime elongation can be found in the formation of the delocalized electronic states. The new HOMO 1 and LUMO 1 levels of CuBM-modified CdS surface (Figure 2b,c) are likely to be located between the valence and conduction bands of CdS. Therefore, they can be populated by the adsorption of the excitonic states of the NP core. The confirmation for that can be clearly seen in the excitation spectrum of this band in the region 350-500 nm [12], which coincides very well with the absorption spectrum of the unmodified NP repeating all its features. The energy gap calculated by DFT for HOMO 1 and LUMO 1 is 1.5 eV. This is also very
close to the energy of the observed red emission of supramolecules; the energy of 700 nm light quantum is 1.76 eV. The 630-750 nm luminescence band also does not show any pronounced size dependence as opposed to the red luminescence of the naked NPs. Altogether, these facts lead to the conclusion that 630-750 nm emission should be mostly attributed to the recombination of electron and hole trapped in LUMO 1 and HOMO 1, respectively. Other donor or acceptor surface states can also be involved in the recombination process with both HOMO 1 and LUMO 1.

What are the consequences of the delocalized nature of the new surface states on the radiative and nonradiative processes in modified NPs? It is known that the delocalization reduces the electronic-to-vibration coupling constant of the transition from the delocalized state to the ground state. Additionally, it reduces the rate of thermally activated transition to the metal-centered states. Both effects decrease the rate of nonradiative processes, which results in a substantial extension of the lifetime of delocalized states, in some cases as much as 3000 times.

Thus, the elongation of the emission lifetime observed for the 630-750 nm band is the natural outcome of the change of the nature of the transition responsible for the red luminescence. Instead of the transition between localized surface traps in naked CdS, the quanta are emitted now due to the transition between delocalized HOMO 1 and LUMO 1 involving the aromatic \( \pi \)-system of the organic ligands in the orbitals.

Now, let us look at the sequence of the calculated energy levels. Besides the delocalized states, there exist HOMOs and LUMOs, which are quite localized. In particular, there are LUMOs preferentially centered on the metal complex side of the supramolecule, which should retain mainly the properties of the corresponding orbitals of the CuBM complex (Figure 2d,e). If the calculated ladder of energy levels in Figure 2 is correct, then the excitation into the higher LUMO states should lead to the subsequent relaxation into LUMO 1, and, after that, the recombination with hole in HOMO 1 can occur which can be seen as the corresponding emission.

5. CONCLUSIONS

The technique of chalcogen modification of NP involves the reaction of the transition metal complex with strong bidentate ligands and weak monodentate ligands. In the course of the reaction, the weak ligand is replaced with a transition metal-chalcogen bond, and the remaining part of the complex becomes attached to the surface of CdS NP. This NP with multiple CuBM units attached constitutes a new type of supramolecular species assembled from qualitatively different chromophores. Molecular orbital calculations and experimental data indicate that surface states delocalized over the NP atoms, transition metal, and \( \pi \)-system of the aromatic orbital develop as a result of the surface modification. Butterfly d-atomic orbitals of the transition metals make possible such bridging, which cannot be realized for surface modification of cadmium sites on CdS NPs. The delocalized surface states strongly affect NP photophysics by altering the carrier dynamics on the surface as demonstrated by the new luminescence features.

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