Interactions of (MY)₆ (M = Zn, Cd; Y = O, S, Se) quantum dots with N-bases

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Abstract

(MY)₆ clusters, with M = Zn and Cd and Y = O, S, Se, form double-layer drum-like structures containing M–Y covalent bonds. The positive regions near the M atoms attract the N atom of both NH₃ and NMe₃ so as to form a noncovalent M···N bond. This bond is quite strong, with interaction energies exceeding 35 kcal/mol. The bond strength diminishes with reduced electronegativity of the Y atom (O > S > Se) and is stronger for M = Zn than for Cd. Trimethylation of the base enhances the bond strength. The interaction is dominated by the electrostatic component which accounts for some 60–70% of the total attractive force. The interaction increases the highest occupied molecular orbital–lowest unoccupied molecular orbital gap by between 0.1 and 0.2 eV.

Keywords Quantum dots · HOMO · LUMO · MEP · DFT · Electron density · σ -Hole

Introduction

Quantum dots (QDs) represent one of the primary frontier subjects of research in the field of nanotechnology. Discovered in 1980 [1], intriguing small nanoparticles (NPs) of diameters in the range of 2–10 nm [2] are characterized by unique physicochemical, electric, and optical properties such as large surface-to-volume ratio, tuneable band gap, diameter-dependent absorption spectrum, and high carrier mobility. These particles are well adapted to play the role of advanced semiconductors and other similar nanoscale devices, and highly useful in a wide range of processes in new technology development, including optical sensing, photocatalysis, energy storage (solar cells), ultrafast optical switches and logic gates, transistors, and even membrane fabrication [3–16].

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Due to their size, the applications of QDs are limited to not only industrial but also biomedical purposes, with possible applications in medical imaging, drug delivery, and biosensing [17–20].

QDs are defined as “containing a variable number of electrons that occupy well-defined, discrete quantum states and have electronic properties intermediate between bulk and discrete fundamental particle” [21]. The designation as “quantum dots” is derived from the notion that their optoelectronic properties are strictly connected with principles of quantum mechanics [21], for example the effect of size on their properties [22]. In general, decreasing the size of the QD crystal increases the difference in energy between the highest valence band and the lowest conduction band, the so-called band gap. Thus, a smaller QD ought to require more energy to excite an electron into the latter band. This effect can be observed as a colour difference that arises in changing the dot size in a given material [21]. The band gap can be tuned via passivation with a ligand or by doping, so as to emit any desired colour of light. The degree of the band gap shift can be described by the Brus quantum mechanics model, taking advantage of the well-known “particle in a box” paradigm [23]. QDs have other interesting features as well, such as broad absorption spectra, high quantum yields, and photochemical robustness [21].

One of the most current and intensively studied nanoparticles within the QD family is the (ZnO)_n nanoclusters. As an isolated molecule, zinc oxide is a wide band gap semiconductor with a direct band gap energy and strong excitation binding

energy. Combining these properties with the high optical transparency and good stability of this entity provides a huge advantage for ZnO in various electro- and opto-derived applications (e.g. light emitting diodes, light detectors, and gas sensors) [24–29]. Several works have described doping procedures applied to various forms of zinc oxide nanoclusters to modify their electrical properties [30–33]. Recently, time-dependent density functional theory (TD-DFT) calculations of (ZnO)₆ nanostructures indicated that substituting O atoms with other chalcogens such as Se or Te atoms offered promise, specifically in biological application [33]. Carbon and sulphur impurities in the (ZnO)₆ structure intensely modulated magnetic properties of this QD and widened its highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) gap [34].

Beside the internal modification of (ZnO)₆, there is also evidence that interaction with a ligand has a powerful impact on QD properties. The mechanism of H₂O adsorption on the (ZnO)_n nanocluster surface was studied by DFT calculations [35, 36] where it was found that the band gap and excitation energy heavily depend on the particular shape of the (ZnO)_n (*n* up to 32) nanocluster. However, adsorption or dissociation of water molecule on the ZnO NP does not introduce substantial changes in these parameters [36]. The authors also discovered that chemisorption is energetically preferred when the Zn atom coordination number is less than four [36]. According to another DFT study concerning adsorption of aliphatic aldehydes on (ZnO)₁₂ clusters, complexation induced considerable changes in the HOMO–LUMO energy gap of the zinc oxide nanocage, which might be useful in sensor design [37]. It was also noted that the adsorption energy decreased upon lengthening the aliphatic chain [37]. Most recently, a series of studies were focused on (ZnY)_n structures (*n* = 6, 28, 30; Y = O, S, Se) [38–41]. The authors found that attaching SO₃ or NO₂ molecules to the hollow cubic and hollow spherical (ZnO)₂₈ or (ZnO)₃₀ QDs increases the HOMO–LUMO gap [38]. They also noted that pyridine passivation of the (ZnO)₆ nanocluster widens the QD band gap more than any other ligand [39]. The theoretical results conformed nicely with available experimental data [38–41].

Other studies have been concerned chiefly with conformational analysis of various QDs [42, 43]. Among various possible configurations of (ZnO)₆, the “drum” (two parallel stacked six-membered rings) conformer is most stable. Another work considered the correlation between morphology and optoelectronic properties of (ZnO)_n and (ZnS)_n for *n* as large as 72 [44]. Other clusters replaced the Zn/O pair by Cd/Se [45–48] as the latter are easy to fabricate, of low-cost, and susceptible to passivation of the active sites. They have, however, a relatively large band gap in their unmodified conformation which has hampered their practical usage to this point [46].

While there has been substantial study of the synthesis strategies, optoelectronic and physical properties of

nanoparticles, and QDs themselves [49–53], the ability of small inorganic molecules to adjust their properties is becoming more evident [34–36, 38–41, 48, 54]. But what is lacking is an understanding of the mechanism by which these perturbations occur. In what precise way do these ligands affect the nanoparticle properties? How might one adjust these perturbations by the proper choice of ligand or of nanoparticle composition and structure? Knowledge of this sort would enable a pathway to the rational design of systems with desirable properties.

As a first step in answering these questions, the current work applies quantum chemical methods to consider a set of small clusters of (MY)₆ type, with both Zn and Cd taken as metals M, one below the other in the periodic table. O, S, and Se were considered as chalcogen atoms Y so as to elucidate the role of atomic size and electronegativity. The interacting ligand was taken as NH₃ as a common N-base; the effects of alkylation were examined by replacing the three H atoms by methyl groups. Such theoretical model is offered as a step toward understanding the much larger nanoclusters that encompass many more atoms. Specifically, the application of σ -hole model to the QD–ligand interactions topic brings new insights into this issue. In order to elucidate the principles underlying the interaction, many of the tools that have been developed to understand σ -hole interactions [55–64] are employed here. While typically applied to small organic and inorganic systems, this style of analysis has found useful application with different sorts of metals as well, as for example gold and platinum nanoclusters [65–71].

As described in detail below, the analysis probes into the nature and magnitudes of the various forces involved in each interaction and their derivation in terms of overall charge distributions and individual orbital interactions. The strengths of individual bonds, covalent as well as noncovalent, are quantified. In addition, the effects of the ligands on the HOMO–LUMO gap are examined in the context of each of these orbitals separate from the other.

Computational details

Geometries of the (MY)₆ (M = Zn, Cd; Y = O, S, Se) QDs and their complexes with ammonia and trimethylamine were fully optimized at the B3LYP-D3(BJ) level in conjunction with the def2TZVPP basis set [72–75]. Another DFT functional, M062X, with the cc-pVTZ basis [76–78] set was also used for geometry optimization and energy calculation to ensure consistency of results. These levels of theory were applied in earlier studies of related QDs and metal nanoparticles [37–40, 42, 79] where they demonstrated their reliability. Harmonic vibrational frequency analysis guaranteed that each optimized structure is a true minimum on the potential energy surface. The interaction energy, E_{int} , of each complex was computed as

the difference in energy between the complex and the sum of monomers within the dimer geometry. E_{int} was corrected for basis set superposition error (BSSE) via the counterpoise procedure [80]. The deformation energies, E_{def} , were evaluated as the difference between the electronic energies of monomers (QD and base) within the complex geometry and the electronic energies of fully optimized isolated monomers.

All procedures which did not require external programs (optimization, frequencies, energies) were carried out using the Gaussian 09 code [81]. Energy decomposition analysis (EDA) was performed at the BLYP-D3(BJ)/ZORA/TZ2P level by the ADF modelling suite using optimized DFT geometries [82–85]. WFA–SAS (Wave Function Analysis–Surface Analysis Suite) was utilized to calculate the MEP (molecular electrostatic potential) on the 0.001 au isodensity surface and to identify its extrema ($V_{\text{s,max}}$ and $V_{\text{s,min}}$) [86]. To assess the possible orbital interactions between the interacting monomers, NBO analysis was performed using version 5.0 of the GenNBO program [87]. DFT electron densities of complexes were analysed via AIMall software in order to find the bond critical points (BCPs) and bond paths [88]. The NCI prescription was used to study the magnitude and exact location of the interaction real spaces between QDs and Lewis bases by means of the MultiWFN and VMD programs [89–91]. The HOMO–LUMO orbitals were illustrated using Chemcraft software [92].

Results

Isolated quantum dots

Earlier work has demonstrated that the drum conformation (two hexagonal ring layers) represents the global minimum geometry of $(\text{MX})_6$ [34, 42, 43]. Our own calculations confirm this preference, with some qualifications. The drum geometry, which is represented by a pair of planar hexagonal rings lying directly above one another, is illustrated in Fig. 1. Note the “staggered” structure in that O atoms lie

directly below M and vice versa. A search of the potential energy surface reveals a number of other minima. As illustrated in Fig. S1, there is a minimum corresponding to a 12-membered single ring, almost but not quite planar. A second structure is somewhat similar but is “pinched in” toward the middle, leading to the close approach of two pairs of Cd/O atoms, labelled here as three 6–4–6 rings. A third minimum is reminiscent of the drum in that there are two layers but differs in that each layer is better described as a pair of four-membered rings than as a hexagon as in the drum. This structure has been dubbed a “cage” in the literature, a designation adopted here as well.

Table S1 indicates the relative energies of these four sorts of structures, optimized at two different levels. M062X/cc-pVTZ verifies the greater stability of the drum, notably lower in energy than the others. On the other hand, B3LYP-D3(BJ)/def2TZVPP suggests that the single ring is more stable than the drum, albeit not by a wide margin. Both levels of theory confirm the much higher energies of the three-ring and cage structures. Given the prevalence of the drum structure in the wurtzite crystalline form [34, 38–40], and its prior examination in numerous publications, along with its predicted existence as global minimum by M062X/cc-pVTZ, it was the drum to which the bulk of the calculations described below are devoted.

Analysis of the molecular electrostatic potential (MEP) of $(\text{ZnO})_6$ in Fig. 2 reveals a regular pattern of positive and negative regions of the $(\text{MX})_6$ systems in general. The most positive of these are located near to the M atoms, extending away from the centre of the drum. The maximum of the potential in this region is designated as $V_{\text{s,max}}$ (a). Another, weaker maximum occurs at the top and bottom of each drum, directly over its centre, and designated as $V_{\text{s,max}}$ (b). The numerical values of these extrema collected in Table 1 obey a number of patterns. Firstly, $V_{\text{s,max}}$ (b) on the tops of the drum centre are significantly weaker than $V_{\text{s,max}}$ (a) by a factor of 2–4. Secondly, the intensity of the positive MEP fades as the chalcogen atom is enlarged and its electronegativity diminished: $\text{O} > \text{S} > \text{Se}$. The Zn-containing QDs have stronger $V_{\text{s,max}}$ (a) than their Cd cousins for any given chalcogen atom Y, but this

Fig. 1 $(\text{ZnO})_6$ and $(\text{CdO})_6$ QDs optimized at the B3LYP-D3(BJ)/def2TZVPP level

Fig. 2 Several views of the molecular electrostatic potential (MEP) of the $(\text{ZnO})_6$ quantum dot, computed on the 0.001 au isodensity contour at the B3LYP-D3(BJ)/def2TZVPP level. Colour ranges, in kilocalorie per mole, are the following: red greater than 40, yellow between 20 and 40, green between 0 and 20, and blue below 0 kcal/mol

pattern is reversed for $V_{s,\text{max}}(b)$ where it is Cd that has the stronger secondary maximum.

While there have been no prior evaluations of the MEP surface of these systems, some comparison may be made with related clusters involving the neighboring coinage metals (Cu, Ag, Au) (also known as “regium” abbreviated as Rg). The σ -holes in Cu_9 , Ag_9 , and Au_9 nanoclusters were of significantly smaller magnitude than those here, ranging between 16.9 and 21.3 kcal/mol [93]. The same metals in smaller Rg_n clusters ($n = 2\text{--}6$) [71] presented larger $V_{s,\text{max}}$ of 208 to 44.1 kcal/mol, still smaller than the higher values observed here.

It is anticipated that the most positive regions of the QDs will interact directly with the negative regions of the two Lewis bases. The $V_{s,\text{min}}$ values for ammonia and trimethylamine are -38.6 and -30.0 kcal/mol, respectively. On the hypothetical basis of a purely electrostatic interaction, one would thus expect NH_3 to form a stronger complex than its trimethylated congener.

Complexes

The optimized geometries of the $(\text{MY})_6$ QDs models complexes with NH_3 and NMe_3 Lewis bases are all exhibited in Fig. S2, with several sample structures displayed in Fig. 3. Although

Table 1 MEP maxima (kcal/mol) on the 0.001 au isodensity surface of $(\text{MX})_6$ QDs, calculated at B3LYP-D3(BJ)/def2TZVPP level

QDs	$V_{s,\text{max}}(a)$	$V_{s,\text{max}}(b)$
$(\text{ZnO})_6$	51.9	19.6
$(\text{ZnS})_6$	46.1	13.1
$(\text{ZnSe})_6$	41.9	10.6
$(\text{CdO})_6$	44.1	24.8
$(\text{CdS})_6$	42.9	22.6
$(\text{CdSe})_6$	40.0	18.9

optimizations were begun with numerous initial positions of the base, all geometries converged on those in Fig. S2, wherein the N atom approached the principal $V_{s,\text{max}}(a)$. In addition to the primary $\text{M}\cdots\text{N}$ interaction, the geometries suggest the possibility of auxiliary $\text{NH}\cdots\text{O}$ or even $\text{CH}\cdots\text{O}$ H-bonds, the influence of which are discussed in detail below.

Some of the chief geometric and energetic aspects of these complexes are reported in Table 2. The intermolecular $\text{R}(\text{M}\cdots\text{N})$ distances are substantially shorter than the sum of Alvarez van der Waals radii [94] of the corresponding atoms which are 405 and 4.15 Å for the $\text{Zn}\cdots\text{N}$ and $\text{Cd}\cdots\text{N}$ pairs, respectively, as would be expected for a significant noncovalent bond. The distances involving Cd are longer than those to Zn, in keeping with the larger radius of the former. The NH_3 is generally a little further from the metal atom than is NMe_3 , by something on the order of 0.01 Å, with the single exception of $(\text{CdO})_6$, which will be discussed below in the context of secondary interactions.

Interaction energies span the range between 20 and 36 kcal/mol. The first obvious trend is the diminishment of interaction energy in the order $\text{Y} = \text{O} > \text{S} > \text{Se}$. The $(\text{ZnY})_6$ complexes are considerably stronger than their Cd counterparts by roughly 4–8 kcal/mol, consistent with the larger values of $V_{s,\text{max}}(a)$ for the former. There is also a clear strengthening (6–8 kcal/mol) that arises from the substitution of the three H atoms of NH_3 by methyl groups. Note that this trend stands in stark contrast to $V_{s,\text{min}}$ which is more negative for NH_3 . The greater stability of NMe_3 dimers may be a consequence of (i) secondary interactions and/or (ii) weakening of the hyperconjugation within the base upon complexation. The latter problem was discussed in an earlier work devoted to the chalcogen bonds in complexes between carbon disulphide and methyl- or chloro-ammonia derivatives [95]. Overall, the complexation energies of these complexes are somewhat weaker than heterodimers of water with ZnO nanocluster³⁶ but stronger than $(\text{ZnO})_m$ ($m = 28\text{--}30$) complexes with CO [38].

The third and fourth columns of Table 2 document the structural distortions undergone by the QDs upon complexation. The primary deformation is the change in the $\text{M}\cdots\text{Y}$ bond lengths for the M atom directly involved in the $\text{M}\cdots\text{N}$ bond. These intramolecular bonds are elongated by something on the order of 0.04 Å, with some variations. For example, the Zn–S bonds in $(\text{ZnS})_6$ show the largest stretches. In concert with the stretch of these two $\text{M}\cdots\text{Y}$ bonds is a reduction in the angle between them of roughly 8°. These geometric changes, along with others, have an energetic consequence. The deformation energies arising in the QD resulting from the complexation are reported in the penultimate column of Table 2. They are not very large, amounting to 1–3 kcal/mol. Even smaller are the deformation energies within the base molecules in the last column, less than 1 kcal/mol. The larger deformations of the Lewis acid as compared to the base are common in interactions such as these [96, 97]. The distortions are not sufficiently large to substantially modify the MEP of the Lewis acid, as has proven to be the case in certain other situations [97].

Fig. 3 Optimized structures of ZnO_6 and CdO_6 complexes with ammonia and trimethylamine

Topology of electron density

So as to better understand the electron density (ED) distribution in these complexes, sometimes referred to as the physical manifestation of the forces in interacting systems [98, 99], an AIM analysis of the topology of the ED distribution was carried out. The bond critical point (BCP) contains a good deal of information about the attractive interaction [100]. These BCPs are indicated by the small green dots in Fig. S3, with the set of systems for $\text{Y}=\text{O}$ displayed as examples in Fig. 4. In addition to the bond paths connecting M with N, some of these systems

also contain bond paths that would suggest H-bonds of various types, viz. $\text{NH}\cdots\text{O}$, $\text{CH}\cdots\text{O}$, $\text{CH}\cdots\text{S}$, and even $\text{CH}\cdots\text{Se}$. However, as explained below, these latter H-bonds would appear to contribute little to the overall stability of these complexes.

A quantitative description of the AIM analysis is summarized by the data in Table 3. First with respect to the density at the BCP, a value of ρ higher than 0.1 au is commonly taken as an indicator of a covalent bond while the 0.002–0.034 range is typical of H-bonds [100]. The values displayed in the third column of Table 3 for the $\text{M}\cdots\text{N}$ bonds range from 0.052 to

Table 2 Structural parameters, interaction energies, E_{int} (corrected for BSSE), and deformation energies, E_{def} of monomers, calculated at the B3LYP-D3(BJ)/def2TZVPP and M062x/cc-pVTZ (in parentheses) levels. Distances in angstrom, angles in degrees, and energies in kilocalorie per mole

Complex	$R(\text{M}\cdots\text{N})$	$\Delta R(\text{M}-\text{Y})^a$	$\Delta\theta(\text{Y}-\text{M}-\text{Y})^b$	E_{int}	$E_{\text{def}}(\text{QD})$	$E_{\text{def}}(\text{LB})$
$(\text{ZnO})_6\cdots\text{NH}_3$	2.083	+ 0.044/+ 0.041	− 8.6	− 29.79 (− 31.86)	1.86	0.09
$(\text{ZnS})_6\cdots\text{NH}_3$	2.111	+ 0.217/+ 0.216	− 9.2	− 27.78 (− 31.60)	2.03	0.07
$(\text{ZnSe})_6\cdots\text{NH}_3$	2.119	+ 0.055/+ 0.055	− 9.0	− 26.54 (− 30.58)	1.93	0.07
$(\text{CdO})_6\cdots\text{NH}_3$	2.319	+ 0.021/+ 0.015	− 8.5	− 25.90 (− 26.99)	2.94	0.46
$(\text{CdS})_6\cdots\text{NH}_3$	2.363	+ 0.044/+ 0.043	− 7.9	− 21.63 (− 24.86)	0.92	0.07
$(\text{CdSe})_6\cdots\text{NH}_3$	2.375	+ 0.039/+ 0.038	− 7.5	− 20.63 (− 24.15)	0.98	0.07
$(\text{ZnO})_6\cdots\text{NMe}_3$	2.075	+ 0.051/+ 0.046	− 8.4	− 36.13 (− 36.82)	2.05	0.83
$(\text{ZnS})_6\cdots\text{NMe}_3$	2.103	+ 0.219/+ 0.217	− 9.1	− 35.56 (− 37.64)	2.16	0.85
$(\text{ZnSe})_6\cdots\text{NMe}_3$	2.116	+ 0.060/+ 0.060	− 9.5	− 34.70 (− 36.89)	2.18	0.86
$(\text{CdO})_6\cdots\text{NMe}_3$	2.325	+ 0.046/+ 0.030	− 8.4	− 28.81 (− 28.75)	1.34	0.74
$(\text{CdS})_6\cdots\text{NMe}_3$	2.353	+ 0.046/+ 0.044	− 7.7	− 28.05 (− 29.44)	0.98	0.59
$(\text{CdSe})_6\cdots\text{NMe}_3$	2.364	+ 0.043/+ 0.043	− 7.6	− 27.29 (− 28.82)	0.83	0.58

^a Difference in $\text{M}-\text{X}$ distances between QD in geometry of complex and fully isolated QD (complex–monomer). The distances of the two closest Y atoms within the same ring to the M atom involved in interaction with Lewis base were considered

^b Angle between M atom involved in $\text{M}\cdots\text{N}$ interaction and two adjacent Y atoms in the same ring

Fig. 4 AIM molecular diagrams showing the bond critical points (green dots) in illustrative $(MO)_6$ complexes with ammonia and trimethylamine. Colours of metal atoms: Zn—violet, Cd—green

0.077 au, stronger than a typical H-bond. In those cases where a secondary H-bond is indicated, the value of ρ is much smaller. The largest of these arises from the $NH\cdots O$ H-bond in $(CdO)_6\cdots NH_3$ of 0.028, less than half the same quantity for the $Cd\cdots N$ bond. The density is much smaller, only 0.008 au for the other auxiliary H-bonds. The AIM analysis suggests then that the interaction energies can be attributed almost completely to the primary $M\cdots N$ bonds. The patterns in the Laplacian of the density in the next column of Table 3 confirm these ideas. Any contributions arising from the secondary interactions are dwarfed by the primary noncovalent bonds. The total electron energy density (H) reinforces this principle and goes one step further in that H is positive for these putative H-bonds, a sign of a very weak bond [100].

The AIM data fit many of the same patterns as observed in the energetics, falling off in the order $O > S > Se$, and the Zn complexes are stronger than their Cd sisters. Methylation of the base increases ρ and H , parallel with the enhanced interaction energy. On the other hand, $\nabla^2\rho$ is less sensitive to the distinction between NH_3 and NMe_3 .

The formation of the complexes also has an internal effect upon the bonding within the QDs. Most important of these are the covalent bonds between the M engaging in the $M\cdots N$ bond and the Y atoms within its same layer (horizontal) and that in the other layer (vertical). The values of both ρ and $\nabla^2\rho$ for each complex are reported in Table 4, followed by the change they each undergo as a result of this complexation. The densities of all of these internal bonds are diminished by the formation of the complex, indicating a bond weakening. This reduction in ρ is consistent with the aforementioned M–Y bond lengthenings indicated in Table 2. $\nabla^2\rho$ follows this trend, but not as consistently, with some bonds showing a very small increase.

Another means of analysing the topology of the electron density arises in the context of the NCI (noncovalent index) approach [89, 90, 101]. The implementation of this technique into the analysis of the complexes of interest here gives rise to the diagrams in Fig. S4 wherein strong attractive interactions are colour-coded as blue regions, and weak interactions such as van der Waals forces

Table 3 AIM descriptors of the bond critical point (BCP) properties: electron density ρ , Laplacian of electron density $\nabla^2\rho$ (both in atomic units), and total electron energy (H , kcal/mol), obtained at the B3LYP-D3(BJ)/def2-TVZPP level

Complex	Interaction	ρ	$\nabla^2\rho$	H
$(ZnO)_6\cdots NH_3$	$Zn\cdots N$	0.072	0.306	−6.61
$(ZnS)_6\cdots NH_3$	$Zn\cdots N$	0.068	0.279	−5.97
$(ZnSe)_6\cdots NH_3$	$Zn\cdots N$	0.067	0.272	−5.72
$(CdO)_6\cdots NH_3$	$Cd\cdots N$	0.058	0.206	−4.82
	$O\cdots H$	0.028	0.093	0.04
$(CdS)_6\cdots NH_3$	$Cd\cdots N$	0.053	0.186	−4.01
$(CdSe)_6\cdots NH_3$	$Cd\cdots N$	0.052	0.180	−3.84
$(ZnO)_6\cdots NMe_3$	$Zn\cdots N$	0.077	0.307	−9.22
$(ZnS)_6\cdots NMe_3$	$Zn\cdots N$	0.073	0.276	−8.43
$(ZnSe)_6\cdots NMe_3$	$Zn\cdots N$	0.071	0.265	−7.94
$(CdO)_6\cdots NMe_3$	$Cd\cdots N$	0.060	0.203	−5.88
	$O\cdots H$	0.008	0.030	0.80
	$O\cdots H$	0.008	0.026	0.73
$(CdS)_6\cdots NMe_3$	$Cd\cdots N$	0.057	0.186	−5.49
	$S\cdots H$	0.006	0.016	0.52
	$S\cdots H$	0.005	0.015	0.51
$(CdSe)_6\cdots NMe_3$	$Cd\cdots N$	0.056	0.180	−5.27
	$Se\cdots H$	0.005	0.014	0.44

Table 4 AIM descriptors (au) of internal covalent bonds in QDs and their change upon complexation with ammonia and trimethylamine at the B3LYP-D3(BJ)/def2-TVZPP level

Complex	Bond within QD	Complex		Complex–monomer	
		ρ	$\nabla^2\rho$	$\Delta\rho$	$\Delta(\nabla^2\rho)$
(ZnO) ₆ ⋯NH ₃	Zn–O (horizontal)	0.090	0.444	−0.012	−0.041
	Zn–O (vertical)	0.058	0.250	−0.010	−0.054
(ZnS) ₆ ⋯NH ₃	Zn–S (horizontal)	0.067	0.162	−0.012	+0.032
	Zn–S (vertical)	0.049	0.115	−0.005	−0.011
(ZnSe) ₆ ⋯NH ₃	Zn–Se (horizontal)	0.059	0.116	−0.007	−0.004
	Zn–Se (vertical)	0.044	0.084	−0.006	−0.010
(CdO) ₆ ⋯NH ₃	Cd–O (horizontal)	0.082	0.347	−0.005	−0.008
	Cd–O (vertical)	0.033	0.115	−0.022	−0.090
(CdS) ₆ ⋯NH ₃	Cd–S (horizontal)	0.063	0.133	−0.006	+0.002
	Cd–S (vertical)	0.038	0.087	−0.004	−0.005
(CdSe) ₆ ⋯NH ₃	Cd–Se (horizontal)	0.056	0.102	−0.005	+0.003
	Cd–Se (vertical)	0.034	0.068	−0.005	−0.006
(ZnO) ₆ ⋯NMe ₃	Zn–O (horizontal)	0.089	0.436	−0.013	−0.049
	Zn–O (vertical)	0.058	0.251	−0.010	−0.053
(ZnS) ₆ ⋯NMe ₃	Zn–S (horizontal)	0.066	0.160	−0.011	+0.030
	Zn–S (vertical)	0.050	0.117	−0.004	−0.009
(ZnSe) ₆ ⋯NMe ₃	Zn–Se (horizontal)	0.059	0.115	−0.007	−0.005
	Zn–Se (vertical)	0.045	0.086	−0.005	−0.008
(CdO) ₆ ⋯NMe ₃	Cd–O (horizontal)	0.079	0.333	−0.008	−0.006
	Cd–O (vertical)	0.046	0.167	−0.009	−0.038
(CdS) ₆ ⋯NMe ₃	Cd–S (horizontal)	0.063	0.133	−0.006	+0.002
	Cd–S (vertical)	0.038	0.087	−0.004	−0.005
(CdSe) ₆ ⋯NMe ₃	Cd–Se (horizontal)	0.056	0.101	−0.005	+0.002
	Cd–Se (vertical)	0.036	0.071	−0.003	−0.003

are indicated by green to light brown and steric repulsions are red. The scatter graphs of the reduced density gradient (RDG) versus the $\lambda_2(\rho)$ parameter are presented next to the coloured isosurfaces maps in Fig. S4. The diagrams verify the presence of the M⋯N interactions as strong noncovalent bonds, i.e. blue regions. There is also some verification provided as to weak secondary interactions in some of these cases.

NBO analysis

The NBO method facilitates an analysis of the contributions to the interaction energy by charge transfers from one orbital to another via second-order perturbation energies, $E(2)$. In the systems considered here, the primary charge transfer involved in the M⋯N bonds originates in the lone pair of the Lewis base N atom and finds its way to the $\sigma^*(M-Y)$ antibonding orbitals of the cluster.

The energetic consequence of that transfer is reported in Table 5, along with the total charge transferred (CT) from the entire Lewis base molecule to the cluster. In general, $E(2)$ is rather large, between 19 and 28 kcal/mol, which verifies the strength of this M⋯N noncovalent bond. The total intermolecular charge shift is also large, more than 0.05 e. Some of the patterns

in Table 5 match the energetic ordering of Table 2. Interactions weaken in the expected $Y = O > S > Se$ order, and Zn⋯N bonds are stronger than their Cd⋯N analogues. On the other hand, the NBO analysis reveals a higher degree of charge transfer for the NH₃ base than for its trimethylated counterpart, opposite to the stronger overall binding of NMe₃. One can conclude then that while charge transfer is an undeniably important factor in the

Table 5 NBO values of the sum of the $E(2)$ orbital interaction energies (kcal/mol) between LP(N) and QD $\sigma^*(M-Y)$ orbitals and total charge transfer (CT, e) from Lewis base to QDs (MY)₆ obtained at the B3LYP-D3(BJ)/def2TZVPP level

Complex	$E(2)$	CT
(ZnO) ₆ ⋯NH ₃	28.10	0.074
(ZnS) ₆ ⋯NH ₃	24.77	0.071
(ZnSe) ₆ ⋯NH ₃	23.71	0.067
(CdO) ₆ ⋯NH ₃	24.88	0.064
(CdS) ₆ ⋯NH ₃	23.18	0.065
(CdSe) ₆ ⋯NH ₃	21.85	0.062
(ZnO) ₆ ⋯NMe ₃	22.41	0.058
(ZnS) ₆ ⋯NMe ₃	19.49	0.052
(ZnSe) ₆ ⋯NMe ₃	18.95	0.050
(CdO) ₆ ⋯NMe ₃	22.92	0.060
(CdS) ₆ ⋯NMe ₃	19.29	0.055
(CdSe) ₆ ⋯NMe ₃	18.54	0.050

noncovalent bonding, it is not decisive in the greater strength arising for the methylated base.

For the most stable complexes with ammonia and trimethylamine, extended analysis of electron density has been performed referring to the orbitals which are involved in the interaction between the QD and Lewis base. The results are collected in Table S3. According to this data, two orbitals are engaged in interaction: antibonding sigma orbitals of (Zn–O) bond and lone electron pair orbital of nitrogen. In ammonia dimer the E(2) interaction energy of 28.10 kcal/mol was found between these orbitals. The $\sigma^*(\text{Zn–O})$ one is formed from an overlap of $sp^{4.59}$ hybrid on O atom (which is a mixture of 18% *s* and 82% *p* atomic orbitals) and the *s* hybrid on the Zn atom (nearly pure *s* type—95%). With respect to the lone pair of N atom, it has $sp^{3.74}$ hybridization (79% *p* and 21% *s* character). In the case of trimethylamine complex, the main difference concerns the hybridization of LP(N) which is nearly pure *p* type (96%). The description of $\sigma^*(\text{Zn–O})$ orbital is very similar to that written for $(\text{ZnO})_6 \cdots \text{NH}_3$ complex as well as occupancies of both orbitals are comparable (about 0.21 e). The amount of interaction energy in the case of complex with NMe_3 is smaller than that in the ammonia complex (22.41 kcal/mol) which is in line with the charge transfer in those complexes.

The values of E(2) and CT measured for these complexes are comparable to those found in the regium bonded heterodimers [71] in which Zn and Cd are replaced by Cu, Ag, and Au. In the case of complexes pairing Ag nanoclusters with ammonia and NCH, E(2) varied from 5.3 to 26.3 kcal/mol and CT lied in the range of 2 to 72 m [71]. In similar sorts of complexes between imidazole and gold nanoparticles, the E(2) energies were also comparable to those evaluated here: 31.5, 23.8, and 8.2 kcal/mol for the two-, four-, and ten-membered Au nanoclusters, respectively [102].

Components of total interaction energy

To gain further insight into the nature of the noncovalent bonding, each interaction energy was decomposed into its

constituent units. The Morokuma–Ziegler method partitions the total into several parts. The electrostatic energy E_{elec} represents the interaction between the unperturbed charge distributions of the two subunits, and E_{oi} contains the interactions between the various orbitals of the two systems, comprising polarization and charge transfer effects, and E_{disp} represents the London dispersion energy.

As is clear from Table 6, the electrostatic component is uniformly the largest in these complexes, comprising some 62–69% of the total attractive energy. This observation is consistent with the parallel nature of the interaction energy and the values of the extrema of the electrostatic potentials of the individual monomer charge distributions. Note also that E_{elec} follows the $\text{O} > \text{S} > \text{Se}$ trend, as well as reflecting the stronger bonding of Zn than Cd, and NMe_3 over NH_3 . In other words, all of the energetic patterns are contained within the electrostatic element. Orbital interactions play an important role as well, but generally less than half as much as E_{elec} , which may account for the trend reversal between interaction energy and NBO charge transfers. Dispersion is a minor factor, accounting for less than 13% of the total. It is uniformly larger for the NMe_3 base than for NH_3 , contributing to the larger interaction energies of the former.

The interaction energy decomposition profile of these complex fits into the overall picture of a wide variety of noncovalent interactions in the literature, even for other decomposition schemes, e.g. SAPT or EDA [71, 95–97, 103–107].

HOMO and LUMO orbitals

The highest occupied molecular orbital and lowest unoccupied molecular orbital (HOMO and LUMO) are the relevant, frontier orbitals which are thought to take part in electrical transport and kinetic stability of a molecular system [108]. The phenomenon of QDs is strongly linked

Table 6 EDA/B3LYP-D3(BJ)/ZORA/TZ2P decomposition of the interaction energy of the complexes into Pauli repulsion (E_{Pauli}), electrostatic (E_{elec}), orbital interaction (E_{oi}), and dispersion (E_{disp}) terms. All energies in kilocalorie per mole. The relative values in percent express the contribution of each to the sum of all attractive energy terms

Complex	E_{int}	E_{Pauli}	E_{elec}	Percent	E_{oi}	Percent	E_{disp}	Percent
$(\text{ZnO})_6 \cdots \text{NH}_3$	−30.96	63.61	−65.64	69	−25.54	27	−3.38	4
$(\text{ZnS})_6 \cdots \text{NH}_3$	−28.64	67.20	−64.22	67	−27.33	29	−4.29	4
$(\text{ZnSe})_6 \cdots \text{NH}_3$	−26.95	69.04	−63.48	66	−27.90	29	−4.63	5
$(\text{CdO})_6 \cdots \text{NH}_3$	−25.95	65.08	−60.94	67	−25.84	28	−4.26	5
$(\text{CdS})_6 \cdots \text{NH}_3$	−22.01	50.01	−49.27	68	−18.84	26	−3.91	5
$(\text{CdSe})_6 \cdots \text{NH}_3$	−20.89	50.73	−48.34	68	−19.06	27	−4.21	6
$(\text{ZnO})_6 \cdots \text{NMe}_3$	−38.19	74.90	−75.45	67	−28.78	25	−8.87	8
$(\text{ZnS})_6 \cdots \text{NMe}_3$	−37.53	80.67	−74.87	63	−31.86	27	−11.47	10
$(\text{ZnSe})_6 \cdots \text{NMe}_3$	−36.44	82.65	−74.01	62	−32.72	27	−12.37	10
$(\text{CdO})_6 \cdots \text{NMe}_3$	−29.25	61.61	−60.07	66	−21.60	24	−9.18	10
$(\text{CdS})_6 \cdots \text{NMe}_3$	−29.05	61.46	−57.74	64	−22.11	24	−10.67	12
$(\text{CdSe})_6 \cdots \text{NMe}_3$	−28.39	62.19	−56.88	63	−22.36	25	−11.34	13

with characterization of their HOMO–LUMO system. The energy gap (E_g) between these MOs is a strong factor in their electron transfer capabilities and thus also their potential semiconductive properties. Earlier work has documented that the attachment of an external molecule to the QD surface can influence this energy gap and consequently the optoelectronic properties of the entire system [38]. The strategy of tuning QDs by binding them in complexes with an assortment of ligands could be used in optimizing the QD's performance.

The effects of the complexation of each QD with the Lewis bases on these orbital energies, as well as their gap, are displayed in Table 7. (The gaps in the uncomplexed monomers are contained in Table S2.) The first two columns of Table 7 show that the interaction with the base raises the energy of both the HOMO and LUMO. But since this energy rise is of larger magnitude for the LUMO, the energy gap is enhanced by some 0.1 to 0.2 eV. There is a general trend for this gap increase to rise in the order $O < S < Se$ and to be larger for Zn than for Cd. The methylation of the base appears to have little effect though.

The last two columns of Table 7 equate the HOMO orbital energy with the ionization potential I (a reflection of Koopman's theorem) and LUMO energy with the electron affinity A . The largest ionization potential of 6.47 au arises for the $(ZnS)_6$ complexes with either base, so these can be considered the most resistant to electron loss. On the opposite end of the spectrum, with the lowest values of $I = 6.05$ eV, are the $(CdSe)_6$ complexes. The highest electron affinity, more than 3 eV is associated with the $(CdO)_6$ systems, which can thus be considered the most electrophilic, with $(ZnS)_6$ the least with $A < 2.4$ eV. To place these quantities in perspective, the electron affinities for isolated Zn and Cd atoms are -0.6 and -0.7 eV, respectively [109].

As a visual supplement to the results in this table, and to provide further context, the HOMO and LUMO orbitals of the $(ZnO)_6 \cdots NH_3$ complex are illustrated as an example in Fig. 5. According to the detailed analysis of canonical molecular orbitals performed for the $(ZnO)_6 \cdots NH_3$ complex, the HOMO orbital is totally localized on $(ZnO)_6$, and it is a mixture of the five lone pair orbitals of four oxygen atoms. The energy of this orbital was calculated as -6.38 eV. The LUMO is localized on the QD mainly, and it is composed of five $\sigma^*(Zn-O)$ NBO orbitals. As one can see in Fig. 5, the LUMO orbital is also slightly localized on the Lewis base. It must be stressed here that according to the analysis, contribution of this orbital (coming from ammonia) is negligible (less than 5% and is not even listed in the NBO output file). The energy of the LUMO was calculated as -2.56 eV, indicating the energy gap between frontier orbitals of 3.83 eV.

The HOMO–LUMO data can be compared with certain prior literature results. For example, the HOMO–LUMO gap reported earlier for the planar form of $(ZnO)_6$ (see Fig. S1) is 2.99 eV [110], considerably smaller than the value calculated here for the drum structure. A gap of 2.91 eV, using the same DFT functional as here, was reported for the much larger $(CdSe)_3$ [46]. Another work [40] considered the effect of doping Co, Fe, and Ni metal atoms into the same set of zinc QDs as discussed here. The gaps for the undoped QDs are close to those reported here, despite the use of a different basis set (LanL2DZ vs def2TZVPP here). The calculations found that E_g increases when the number of Co dopants is odd, or when the number of Fe atoms increases, but smaller changes were observed in other cases. Doping by C atoms [34] lowered the gap but the reverse was observed for S atoms.

Perhaps more to the point is the effect of interactions with external ligands. CO, NO₂, and SO₃ molecules produced varied effects on E_g depending upon the specific binding site of

Table 7 Changes in orbital energies resulting from complexation with indicated Lewis base, along with energetics of electron removal and attraction from the QD. (All data in eV)

Complex	ΔE_{HOMO}	ΔE_{LUMO}	$\Delta E_{HOMO-LUMO}$ gap	First ionization potential (I)	Electron affinity (A)
$(ZnO)_6 \cdots NH_3$	+0.56	+0.65	+0.10	6.38	2.56
$(ZnS)_6 \cdots NH_3$	+0.42	+0.59	+0.18	6.47	2.39
$(ZnSe)_6 \cdots NH_3$	+0.37	+0.55	+0.19	6.26	2.45
$(CdO)_6 \cdots NH_3$	+0.32	+0.44	+0.12	6.20	3.21
$(CdS)_6 \cdots NH_3$	+0.36	+0.47	+0.11	6.20	2.76
$(CdSe)_6 \cdots NH_3$	+0.30	+0.44	+0.13	6.05	2.75
$(ZnO)_6 \cdots NMe_3$	+0.55	+0.67	+0.12	6.39	2.54
$(ZnS)_6 \cdots NMe_3$	+0.42	+0.62	+0.19	6.47	2.36
$(ZnSe)_6 \cdots NMe_3$	+0.38	+0.58	+0.20	6.25	2.42
$(CdO)_6 \cdots NMe_3$	+0.44	+0.55	+0.11	6.08	3.10
$(CdS)_6 \cdots NMe_3$	+0.35	+0.50	+0.13	6.21	2.75
$(CdSe)_6 \cdots NMe_3$	+0.30	+0.45	+0.14	6.05	2.73

Fig. 5 HOMO and LUMO orbitals of the $(\text{ZnO})_6 \cdots \text{NH}_3$ complex on the 0.03 au isodensity contour computed at the B3LYP-D3(BJ)/def2-TVZPP level. Pink and purple colours refer to opposite signs of the wave function

$(\text{ZnO})_m$ ($m = 28\text{--}30$) QDs [38]. The greatest gap reduction was associated with the placement of NO_2 and SO_3 molecules in the centre of the hollow cubic or hollow spherical ZnO QD. More closely akin to our own systems, another DFT study [39] of passivation of $(\text{ZnO})_6$ nanoclusters by ammonia, methanol, methylamine, and pyridine ligands led to the same observation as found here—the band gap widens with ammonia ligand capping, no matter the site of attack. The other ligands resulted in band gap variation but with patterns that were less than clear. Finally, it has been found that water molecule adsorption on numerous ZnO QDs yields only small changes in these energy gaps [36].

Conclusions

In summary, $(\text{MY})_6$ quantum dot models engage in strong $\text{M} \cdots \text{N}$ noncovalent bonds with N-bases. The interaction energies are quite large, as much as 36 kcal/mol. The interaction is comprised to a large extent of a Coulombic attraction which accounts for as much as 70% of the total attraction. This force is supplemented by a smaller component derived from orbital interactions and an even smaller dispersive attraction. Zn engages in a stronger $\text{M} \cdots \text{N}$ bond than does its Cd counterpart below it in the periodic table, and the interaction weakens with diminishing electronegativity of the chalcogen atom $\text{Y} = \text{O} > \text{S} > \text{Se}$. Replacement of H atoms of the NH_3 base by methyl groups enhances the binding as well. Most of these trends are accurately reproduced by

electrostatic potentials, AIM analysis of the electron density topology, and NBO measures of charge transfer. But the latter would incorrectly predict a stronger $\text{M} \cdots \text{N}$ bond for NH_3 as compared to NMe_3 , as would a simple comparison of electrostatic potentials.

There is relatively little monomer geometric deformation that accompanies the complexation, amounting to only 3 kcal/mol or less. The deformations involve chiefly the lengthening of some of the internal $\text{M} \cdots \text{Y}$ covalent bonds within the QD, coupled with reduction in the associated $\text{Y} \cdots \text{M} \cdots \text{Y}$ bond angles. The complexation of the QD with a base increases the HOMO–LUMO gap by some 5% which will have an effect on its conductivity properties. It is hoped that the results presented here may steer future work related to the development of the new QDs–ligand complexes and the rational design of materials with desired properties based on these superbly tuneable nanoparticles.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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