PCCP

PAPER

Check for updates

Cite this: Phys. Chem. Chem. Phys., 2019, 21, 589

Received 7th October 2018, Accepted 27th November 2018

DOI: 10.1039/c8cp06235h

rsc.li/pccp

Introduction

The surface plays a significant role in the overall physical and chemical properties of a colloidal quantum dots (Qdots).^{1–15} This recognition has led to the development of methods such as passivation as well as functionalization with organic and inorganic ligands and core–shell formation in achieving the desired objectives.^{1–6} Moreover, there is a demand for novel multifunctional materials formed out of Qdots and other moieties, which are endowed with the synergistic action of the components.^{7–9} These new and improved materials may find important applications in energy, environment and healthcare.

We have recently proposed and demonstrated that inorganic complexes could be formed on the surface of a Qdot *via* the reaction of a cation, with externally added ligands being present in the dispersion medium.¹⁰ This has led to the generation of new optical properties, such as white light-generation from a single particle, involving the Qdot and the surface complex.^{11,12} Interestingly, the surface anion provides additional chemical and

The nature of binding of quinolate complex on the surface of ZnS quantum dots[†]

Shilaj Roy, 🕒 ^a Satyapriya Bhandari, ២ ^b Mihir Manna, ^a Suranjan De^a and Arun Chattopadhyay 🕩 *^{ab}

We report that the Z-type binding rather than X-type binding was favored when 8-hydroxyquinoline (HQ) reacted with presynthesized ZnS quantum dots (Qdots) to form surface zinc quinolinate complexes having a preferred stoichiometry of 1:2 (surface Zn^{2+} :HQ). Importantly, the higher solubility in polar solvents and high desorption coefficient (following Langmuir binding isotherm) of HQ-treated ZnS Qdot in DMSO solvent compared with those in methanol clearly indicated the favorable Z-type binding of HQ and thus the formation of surface octahedral ZnQ₂ complex. Furthermore, the characteristics peaks in the ¹H-nuclear magnetic resonance (NMR) spectrum of the desorbed species and the ligand density calculation of the surface complex (formed due to the reaction between HQ and ZnS Qdot) supported the octahedral ZnQ₂ complex on the surface of ZnS Qdots (in turn gaining structural rigidity) may be the reasons for the Z-type binding of HQ. The specific binding might be the reason for superior optical properties and thermal stability of the surface ZnQ₂ complex compared to the free ZnQ₂ complex as such. The results can be considered important towards understanding the coordination chemistry of inorganic complex on the surface of Qdots and thus for their application potential.

thermal stability to the complex.^{13,14} For example, the reaction between 8-hydroxy quinoline (HQ) and ZnS based Qdots led to the formation of a surface ZnQ_2 complex with enhanced optical and thermal stability properties. The new composite material has been defined as a Qdot complex (QDC). Furthermore, exchange of surface complexes between two Qdots – based on the superior chemical stability of one over the other – has also been observed.¹⁴

An important aspect of surface complexation is the structure of the complex on the surface vis-à-vis that in the dispersion medium or in its crystalline form. Any new aspect of the properties would depend on the binding of the complex with the surface ion(s) and its geometric structure on the surface. In this regard, based on the binding modes on the surface of a Qdot, more particularly on the electron donating capability in neutral form, organic ligands can be classified into three categories: L-type (two electron donor), X-type (one electron donor) and Z-type (electron acceptor).^{15–19} Among them, the attachment and stability of X and L type ligands occur via free metal ions on the surface of a Qdot, while Z-type ligand binding is assisted by dangling anions on the surface.^{16–19} Similarly, the nature of binding of the inorganic complex on the surface is expected to depend on its native structure and (primarily) surface anions, with which the central metal ion may coordinate.

In this regard, while our recent studies have indicated the advantages of systematic surface functionalization, a comprehensive understanding of the binding chemistry and surface

ROYAL SOCIETY OF CHEMISTRY

View Article Online

^a Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati-781039, Assam, India. E-mail: arun@iitg.ernet.in;

Fax: +91-361-2582349; Tel: +91-361-2582304

^b Centre for Nanotechnology, Indian Institute of Technology Guwahati, Guwahati-781039, Assam, India

 $[\]dagger$ Electronic supplementary information (ESI) available: Fig. S1–S11 and Table S1. See DOI: 10.1039/c8cp06235h

coverage of complexes involving ligands such as HQ and ZnS Qdots is yet to be explored. This is deemed important in order to foster further growth of multifunctional nanomaterials at the highest spatial resolution.

Herein, we report that the complexation reaction of HQ with ZnS Qdot - with the formation of QDC - possibly involves formation of a Z-type surface zinc quinolate complex with stoichiometry of 1:2. Importantly, the solvent-dependent Langmuir adsorption isotherm revealed that the moiety desorbed from the QDC surface was highly soluble in DMSO, similar to a normal ZnQ₂ complex. Furthermore, the dispersibility of QDC in polar solvents (such as water-alcohol mixture and DMSO) indicated the presence of a polar interaction site, which is akin to that of a normal ZnQ₂ complex. This projected the octahedral ZnQ₂ complex as a Z-type capping ligand of QDC. Additionally, the resemblance in ¹H-NMR signals of the supernatant obtained after centrifuging the QDC dispersion with that of a normal zinc-quinolato complex further suggested the presence of zinc-quinolato complex as a desorbed species that binds with the surface as an adsorbed species. Furthermore, the footprint area and corresponding density of the zinc quinolate complex on the surface of the ZnS Qdot were found to be similar to that of the area required for octahedral ZnQ₂. The observed similar emission maximum of QDC (i) with that of bare ZnQ₂ complex (in solid state) and (ii) and that of the product formed out a reaction between ZnS and a tetra dentate ligand L1 (which can form complex with Zn²⁺ similar to that of ZnO₂ type) also indicated the formation and attachment of Z-type ZnQ₂ on the surface of the ZnS Qdot.

Experimental

Synthesis of ethylene diamine capped ZnS quantum dots

Synthesis of ethylene diamine-capped ZnS quantum dots (Qdots) has been performed by following a reported protocol.¹³ First, 0.25 millimole of zinc acetate dihydrate (Zn(OAc)₂·2H₂O) was added to a 100 mL round bottom flask containing 50 mL water – placed on a hotplate under stirring condition. Next, 500 μ L of ethylene diamine and 0.25 millimole of sodium sulphide were sequentially added to the above solution. Then, the solution was refluxed for 2 h and the temperature was fixed at 393 K. Following this, an opaque milky white dispersion was observed and it was centrifuged at 25 000 rpm for 15 min. To remove all the unreacted salts, the obtained pellet was redispersed in water and centrifuged. The washing process was repeated twice and then, the product was further washed by methanol. Finally, the as-obtained pellet was redispersed in 200 mL of methanol and used for performing the experiments.

Calculation of concentration of ZnS quantum dots

From particle size distribution of TEM analyses, the average diameter of a ZnS Qdot was calculated to be $d = 3.37 \pm 0.3$ nm (Fig. S1, ESI†). Consequently, the average radius was calculated to be $r \approx 1.685$ nm. Therefore, considering each single Qdot to be a sphere, the volume of a ZnS Qdot sphere was calculated to

be, $\frac{4}{3}\pi r^3 = 20.04 \times 10^3 \text{ Å}^3$ and the surface area of a ZnS Qdot was found to be A = $4\pi r^2 = 3.57 \times 10^3 \text{ Å}^2$. Now, from the diffraction pattern, it was found that the lattice structure of the ZnS Qdot (ethylene diamine capped) was wurtzite (Fig. S1, ESI†).¹³ As a single ZnS wurtzite cell has a volume of $a = 79.11 \text{ Å}^3$, a single ZnS Qdot consists of 253 (*i.e.*, V/*a*) units of wurtzite cells. It is important to mention here that a unit ZnS wurtzite cell consists of 2 Zn²⁺ ions. Hence, the number of Zn²⁺ ions per single ZnS Qdot is 506. From AAS analyses, the total concentration of Zn²⁺ in the as-prepared Qdot dispersion was found to be 0.9 mM. Hence, the concentration of ZnS Qdot in the as-prepared Qdot dispersion was (0.9/506) mM = 1.77 μ M.

Calculation of ligand density

For calculating the density of 8-HQ on the surface of a ZnS Qdot and the footprint area of 8-HQ on the surface of a ZnS Qdot, ZnS Qdots in methanolic medium (*i.e.*, methanol- d_4) were reacted with slightly excess 8-HQ (which was determined from the titration of 8-HQ and ZnS Qdots) and the amount of unreacted 8-HQ was determined by NMR spectroscopy. Consequently, the attached amount of HQ was calculated by subtracting the unreacted amount from total amount of 8-HQ. For this experiment, we have taken 1/8th part of ZnS Qdot (i.e., 25 mL as synthesized ZnS Qdot) from one-time-performed synthesis (5 mM 50 mL scale synthesis - as described before) and centrifuged to obtain the pellet. Then, the solvent was evaporated and the dried pellet was redispersed in 500 µL of methanol-d₄. Following this, 30 μ L of 50 mM of HQ (in methanol-d₄) was added to that Qdot dispersion. Additionally, 10 µL stock solution of DMSO (*i.e.*, 5 μ L DMSO in 500 μ L methanol d₄) was added to that dispersion as an internal standard. NMR spectra (Fig. S2 and S3, ESI[†]) of the mixture were recorded and absolute integration values for each peak corresponding to 8-HQ and DMSO were calculated. NMR spectrum of 500 µL of 1 mM HQ in methanol-d4 (added with same amount of internal standard) was used as the reference standard. From the integrated areas under the curves in the NMR spectra, the amount of free ligand (50 mM HQ) in the sample was found to be 3.52 µL, while the amount of attached ligand is 26.48 µL. Consequently, the number of ligands per Qdot is 29.4 (\approx 30). Hence, the number of 1:2 complex (ZnQ₂) units per Qdot is 15. Thus, the footprint area per complex is 2.38 nm^2 and footprint per ligand is 1.19 nm².

Synthesis of L1

Ligand L1 was synthesized by a two-step reaction as per the reported protocol (Scheme 1).²⁰ First, 2-chloro-*N*-(quinol-8-yl)-acetamide was synthesized by the reaction between 2-chloro-acetyl chloride and 8-aminoquinoline. Then, 20 mmol of 8-aminoquinoline and ~3.0 mL of Et₃N were dissolved in 15 mL of chloroform in a round bottom flask and maintained at low temperature (*i.e.*, <277 K) under vigorous stirring. Following this, ~5.5 mL of 2-chloroacetyl chloride (dissolved in 10 mL of chloroform) solution was poured dropwise to the above solution for ~30 min and the reaction mixture was kept under the same conditions for 3 h. Then, the solvent mixture was evaporated by reducing the pressure using a vacuum pump



Scheme 1 Schematic of synthetic route of ligand L-1.

to a obtain white solid, which was purified by column chromatography (silica gel) using dichloromethane as the eluent to obtain pure chloro-*N*-(quinol-8-yl)-acetamide.

Next, chloro-*N*-(quinol-8-yl)-acetamide was used to prepare *N*-(quinolin-8-yl)-2-(quinolin-8-yloxy)acetamide (L1). For this purpose, 5.0 mmol of chloro-*N*-(quinol-8-yl)-acetamide, 5.0 mmol of 8-hydroxyquinoline (8-HQ), ~900 mg of K₂CO₃ and ~10 mg of KI were mixed in ~30.0 mL of DMF in a round bottom flask. Following this, the reaction mixture was stirred vigorously under reflux for ~12 h. After completion of the reaction, the reaction mixture was cooled to room temperature. The solvent was removed by evaporation under reduced pressure. Pure *N*-(quinolin-8-yl)-2-(quinolin-8-yloxy)acetamide (L1) was collected after performing silica gel column chromatographic separation. The as-synthesized L1 was characterized by using NMR and mass spectrometry (Fig. S4 and S5, ESI†) (Scheme 1).

Instruments

(i) 600 MHz nuclear magnetic resonance (NMR) spectrometer (Bruker) (ii) Agilent Accurate Mass (LC/MS Q-TOF 6520) spectrometer (iii) Perkin Elmer LAMBDA 750 UV/Vis/NIR spectrophotometer and (iv) HORIBA Jobin Yvon FluoroMax-4 spectrofluorimeter, (v) JEOL JEM-2100 transmission electron microscope (maximum accelerating voltage 200 kV), and (vi) Perkin-Elmer (Model: Spectrum Two) FTIR spectrophotometer, and (vii) Bruker D8 X-ray powder diffractometer were used.

Results and discussion

Formation and characterization of QDC

Ethylene diamine-capped ZnS Qdots with an average particle size of 3.35 \pm 0.3 nm were synthesized based on a previously reported protocol.^{13,14} Further details of analytical characterizations are included in the ESI[†] (Fig. S1). The ethanolic dispersion of the as-synthesized ZnS Qdots showed an absorption edge at 320 nm and a broad emission peak centered at 440 nm, which is typical of emission from surface trap states^{14,15} (Fig. S1D, ESI[†]). The treatment of HQ with the ZnS Qdots resulted in the formation of a new luminescent nanocomposite, the absorption spectrum of which comprised two peaks at 320 nm (due to ZnS Qdots) and 365 nm (appeared due to the formation of surface Zn-quinolate complex).^{10,13,14} In the emission spectrum, the peak due to the Qdot disappeared and a new peak at 500 nm appeared (Fig. S6D, ESI†). Additionally, the emission spectrum of QDC exhibited an excitation peak at 365 nm when probed with an emission maximum at 500 nm,

while the emission spectrum of only ZnS Qdots showed an excitation peak at 320 nm upon probing with an emission maximum at 440 nm (Fig. S7, ESI[†]). There was no significant change in terms of the size and structure (*i.e.*, lattice fringe) of ZnS Qdots¹³ in the QDC, as observed in the TEM (and corresponding particle size distribution) and high resolution TEM (and IFFT) (Fig. S6A–C, ESI[†]). Importantly, the presence of the characteristic peaks in the FTIR spectrum of the functional group of the zinc quinolate complex¹⁰ in QDC also ESI[†] (Fig. S8 and Table S1).

Our earlier observations suggested that when HQ reacted with ZnS Qdots, the formation of a product on the surface of the Qdots with properties akin to ZnQ_2 complex was favored.^{10,13} This was further supported by the reaction of ZnQ₂ with ZnS Qdots, leading to a product with similar properties. In addition, it was observed that thermal stability and photostability of the ZnQ₂ complex was enhanced when attached to the surface of the Qdots. The results also indicated important roles of surface sulphide ions and Zn^{2+} ions in the stability of the complex and reactivity of the Qdots. These findings bring us to the question on the nature of the surface species and their properties in a dispersion medium.

Dispersibility and stability of dispersion

An important first test of the nature of the species present on the surface of the Qdots could be the ability to disperse in a liquid medium. This will depend not only on the nature of the ligand attached to the surface but also on the mode of the attachment. Considering Green's classification, HQ - a bidentate chelating ligand - can be classified as an LX-type ligand as it has two parts - one is pyridyl (i.e., L-type) and the other is phenolic (*i.e.*, X-type).¹⁵ Consequently, two possible modes can be anticipated for binding of HQ to the surface of the ZnS Qdot, namely, (i) 1:1 binding - where one HQ moiety binds with a surface Zn^{2+} ion by X-type binding, which can be visualized as cation capping and (ii) 1:2 binding - where two HQ moieties bind with Zn²⁺ to form ZnQ₂ complex, which would be attached to the ZnS surface through dangling sulfides - visualized as anion capping. In this regard, the dispersibility and corresponding stability (as measured through the luminescence at 500 nm; Fig. 1A and B) of the dispersion of QDC (HQ treated ZnS Qdot) in different solvents (namely, (i) MeOH, (ii) MeOH-H2O, (iii) DMSO, (iv) H₂O and (v) hexane) were tested. The QDC was found to be dispersible in polar media and the dispersions exhibited high stability in DMSO and MeOH solvent systems among the five solvent systems of interest. This is reflected in the bar diagram of the ratio of the luminescence intensities of the dispersion of QDC in different solvents at 500 nm at time intervals of 20 h to 0 h (Fig. 1B). It should be mentioned here that QDC was hardly dispersible in nonpolar solvents such as hexane. Thus, if 1:1 binding mode (X type) or perpendicular stacking of the ligand HQ on the surface of Qdot was favored over 1:2 binding mode (Z type), then the outer surface of the QDC might have consisted of exposed non-polar hydrophobic ends of HQ (as is visualized in Fig. 1C(i)). This would have rendered the QDC dispersible in nonpolar solvents such as



Fig. 1 (A) Emission spectra ($\lambda_{ex} = 365$ nm) of the same amount of QDC (*i.e.*, HQ added ZnS Qdots) after dispersing in different solvents: (i) DMSO (ii) MeOH (iii) MeOH-H₂O (iv) H₂O and (v) hexane. (B) Bar diagram of the ratio of luminescence intensity (at 500 nm) of the QDC recorded at time interval of 20 and 0 h in different solvents: (i) DMSO (ii) MeOH (iii) MeOH-H₂O (iv) H₂O and (v) hexane. (C) Schematic of (i) 1:1 and (ii) 1:2 binding modes of HQ to the surface Zn²⁺ of ZnS Qdot.

hexane by virtue of non-polar interactions. However, the affinity of the QDC towards polar solvents supports the presence of sites for polar interaction in the outer ligand shell of the QDC. This can be explained through the Z-type binding (*i.e.*, 1:2 complex binding) mode of the ligand on the surface, which further points towards octahedral or distorted octahedral complex, in which the axial sixth coordination may be responsible for polar interactions with the solvent molecule (Fig. 1C(ii)). Hence, the trends in dispersibility and stability of the dispersion indicate the binding of ZnQ_2 complex on the surface of Qdot *via* dangling sulphide bonds as an axial fifth coordination species (as visualized in Fig. 1C(ii)). The other axial coordination point of the complex might have been occupied by the solvent molecule,²¹ thus accounting for the dispersibility as well as stability of QDC in a particular solvent. This is further supported from our earlier results of complexation-assisted phase transfer of hydrophobic Qdots from nonpolar to polar medium.²²

Solvent dependent adsorption of HQ on the surface of ZnS Qdot

Next, we investigated the nature of binding of the ligand (HQ) on the surface of a Qdot based on the evolution of PL emission (centered at 500 nm) originating from surface zinc quinolato complex upon addition of HQ to the dispersion of ZnS Qdot in two different solvent systems (DMSO and MeOH). In case of PL emission in DMSO, appearance of an additional peak at \sim 440 nm may be because of weak luminescence of DMSO observed at low QDC concentration, which is absent in case of MeOH (Fig. 2A). Since at considerably low concentrations of emitting species, the emission intensity is directly proportional to the concentration of that species, the intensity at 500 nm directly indicates the amount of the formed surface quinolato complex. Furthermore, based on earlier observations,^{13,14,23-25} we made the following additional assumptions in this regard: (i) at very low concentration, ligand(HQ) is completely bounded



Fig. 2 (A) Emission spectra (λ_{ex} – 365 nm) of the different amount of HQ ([HQ] = 0.3 mM for MeOH; [HQ] = 1.0 mM for DMSO and the amounts of HQ added have been mentioned in legend) added ZnS Qdots (0.177 μ M 3.0 mL Qdot dispersion), in (i) MeOH and (ii) DMSO, respectively, as solvents. (B) Plot of surface coverage vs. concentration of free HQ and corresponding (C) reciprocal plot of Langmuir binding isotherm with a linear fitting in (i) MeOH and (ii) DMSO solvents, respectively.

to the surface of ZnS Qdot and thus, no free ligand is present; (ii) surface coverage may be considered to be '1' when ZnS Qdot was treated with a high amount of HQ. Using PL spectroscopy, we monitored the reaction between HQ and ZnS Qdots in both MeOH and DMSO media (Fig. 2A). Primarily, we investigated whether binding of HQ on the surface of ZnS Qdot followed Langmuir isotherm in both the solvents (i.e., MeOH and DMSO). From Fig. 2B and C, it is evident that binding of HQ on the surface of ZnS Qdot can be treated as an adsorption phenomenon that follows Langmuir isotherm with better agreement in case of MeOH compared to DMSO. The surface complexation phenomenon can be speculated as adsorption of HQ on the surface of ZnS Qdot following the formation of surface zinc quinolato complex - more precisely, complexation assisted adsorption. Upon formation of zinc quinolato complex (possibly, ZnQ₂) on the surface, desorption can possibly occur either in the form of ZnQ₂ or as the quinolato moiety itself. However, the desorption of a particular species is dependent on the solubility of that species in a solvent medium. Owing to the higher solubility of ZnQ₂ in DMSO than in MeOH, the extent of desorption of the Z-type surface ZnQ₂ complex would be much higher in case of DMSO. The other possible path of desorption, i.e., desorption of quinolato moiety by means of dissociation of complex, may be considered as a part of complexation equilibrium. Hence, in MeOH only dissociation-assisted desorption of quinolato moiety was prevalent. However, in case of DMSO, Z-type complex desorption as well as desorption of quinolato moiety occurred, although Z-type desorption may be the primary pathway in comparison to dissociation of a chelating complex.

Adsorption model of the surface complexation reaction

Based on the discussions, a model can be proposed for better understanding of the ligand binding phenomenon. The reaction can be visualized as two-step process:

(i) Adsorption of HQ followed by complexation on the surface of ZnS Qdot (formation of 1:2 complex with surface cation):

Surface
$$-Zn^{2+} + 2HQ \xrightarrow[k_d]{k_d}$$
 surface $-ZnQ_2$ (1)

(ii) Adsorption equilibrium between adsorbed complex and desorbed complex (Z-type ligand binding):

Surface
$$-ZnQ_2 \xrightarrow[k_a]{k_a'}$$
 desorbed $-ZnQ_2$ (2)

Now, HQ is attached on the surface the Qdot *via* the formation of a luminescent ZnQ_2 complex. Thus, the surface coverage of Qdot can be expressed as a function of PL intensity as follows:

$$\theta = \frac{I}{I_{\text{max}}} \tag{3}$$

where θ = average surface coverage, and I_{max} = maximum fluorescent intensity, which was determined using highly concentrated HQ.

Paper

Now, considering the two step reaction the surface equilibrium can be expressed as

$$k_{\rm a}(1-\theta)[{\rm HQ}] + k_{\rm a}'(1-\theta)[{\rm ZnQ}_2] = k_{\rm d}\theta + k_{\rm d}'\theta \qquad (4)$$

As free ZnQ_2 is the intermediate species and HQ is added to the mixture externally, we have $[HQ] \gg [ZnQ_2]$. Thus, the equation can be written as

$$k_{\rm a}(1-\theta)[{\rm HQ}] = (k_{\rm d} + k_{\rm d}')\theta \tag{5}$$

Hence,

$$\theta = \frac{K_{ca}[HQ]}{K_{ca}[HQ] + 1};$$
 where $K_{ca} = \frac{k_a}{k_d + k_d'}$ (6)

We term the new constant ' K_{ca} ' as complexation adsorption constant. k_a/k_d is similar to surface complexation constant. Thus, ' K_{ca} ' herein represents the adsorption constant (K). Importantly, 'Kca' takes care of the complexation-assisted adsorption of HQ as well as solubility driven desorption of ZnQ₂, occurring simultaneously on the surface. Due to higher solubility of ZnQ2 in DMSO than in MeOH, the extent of desorption would be higher in case of DMSO. As a result, desorption coefficient of ZnQ2 in DMSO would be much higher than that of MeOH, $[(k_d')_{\text{DMSO}} \gg (k_d')_{\text{MeOH}}]$ – which would result in the lower value of 'K_{ca}' in DMSO than in MeOH (*i.e.*, for 0.177 μ M ZnS Qdot, $(K_{ca})_{MeOH}$ = 2.61 \times 10⁸ M⁻¹ and $(K_{ca})_{DMSO}$ = $1.18 \times 10^8 \,\text{M}^{-1}$, which were obtained from the value of '1/slope' in Fig. 2C). The assumption that $[HQ] \gg [ZnQ_2]$ may not be accurate in the case of treatment of ZnS Qdot with low concentration of HQ in DMSO solvent. In this concentration range, the extent of complex formation is high (based on Le Chatelier's principle) and desorption of Z-type ZnQ₂ complex may also occur. Thus, the deviation from simple Langmuir isotherm in case of DMSO is possible. Therefore, the above model projects the zinc quinolato complex (or, ZnQ_2) as the attached species and thus supports Z-type (1:2) binding of HQ to the surface of the ZnS Qdots. However, this finding requires further experimental substantiation.

Identification of the desorbed species by NMR spectroscopy

The desorption of zinc-quinolato complex from the surface of QDC in DMSO was substantiated by NMR spectroscopic analysis. The supernatant obtained by centrifugation of QDC dispersion in DMSO-d₆ was used for ¹H NMR analyses. Notably, when the complexation reaction of HQ with Zn²⁺ ions in a liquid medium (DMSO) was performed, a shift in the characteristic peaks of HQ was observed (Fig. 3). For example, the characteristic peak of HQ at 7.1 ppm (which was assigned to proton number 6) shifted to 6.88 ppm following complexation with Zn^{2+} ions (*i.e.*, the formation of normal ZnQ_2 complex; Fig. 3). Interestingly, the supernatant of the HQ-treated ZnS Qdot (QDC) exhibited characteristics peaks at 6.88 (for the proton number 6 of HQ), which is akin to that of ZnQ₂ complex (Fig. 3). This clearly indicated the presence of ZnQ_2 complex in the supernatant of the HQ-treated ZnS Qdot (QDC). Moreover, the additional peaks present in the NMR spectrum of

Paper



Fig. 3 ¹H nuclear magnetic resonance (NMR) spectra of (i) only HQ (in d₆-DMSO), (ii) only ZnQ₂ (in d₆-DMSO) and (iii) supernatant of HQ treated ZnS Qdots (obtained following centrifugation of the as-synthesized product and redispersion in DMSO-d₆). The peaks representing aromatic ¹H of the spectra (δ = 6.5–9 ppm) are highlighted by dotted ellipses.

supernatant of HQ-treated ZnS Qdot may be attributed to the presence of HQ and impurity in the supernatant solution. The detailed spectral analyses have been produced in the ESI \dagger (Fig. S9–S11). Thus, the results indicated zinc-quinolato complex as the desorbed species, which might have been attached to the surface reversibly as a consequence of adsorption equilibrium. Thus, the structure of the surface zinc quinolate complex (*i.e.* the desorbed species of the HQ treated ZnS Qdots) can be anticipated as octahedral or distorted octahedral ZnQ₂ with one axial position occupied by the dangling sulphide bond (which helps in the stabilization and attachment of the complex on the surface of a ZnS Qdot) and the other axial position occupied by one solvent molecule (here DMSO, which defines the higher solubility of the Qdot in the polar solvents).

Solid state photoluminescence and attachment of L1

It is to be mentioned here that the emission maximum (at 500 nm with an excitation wavelength of 365 nm) of the QDC was similar to that of ZnQ_2 complex in solid form (Fig. 4A). The electronic transition from the electron rich phenoxide ring (HOMO; highest occupied molecular orbital) to the electron deficient pyridyl ring (LUMO; lowest occupied molecular orbital) may account for the origin of the luminescence of the QDC.²⁶ Additionally, when a modified ligand of HQ (L1) – with the ability to form distorted pentagonal luminescent crystal with normal Zn^{2+} ions – was used for complexation on the surface of ZnS Qdots, the newly formed QDC showed a similar emission in the solid form (*i.e.*, at 500 nm, with an excitation wavelength of 365 nm; Fig. 4B). These results also indicated that when HQ reacted with ZnS Qdot, the formation of 1:2 binding mode (Z type: ZnQ₂ complex with octahedral/distorted

Fig. 4 Solid State emission spectra (λ_{ex} = 365 nm) of (A) QDC and (inset) only ZnQ₂. (B) Emission spectra (λ_{ex} = 365 nm) of L1 treated ZnS Qdots obtained following centrifugation (and then redispersion in MeOH).

octahedral structure) was preferred over 1:1 binding mode. Thus, the dangling sulphide accounted for the stabilization of the ZnQ_2 complex on the surface of ZnS Qdots (following replacement of the existing (as-synthesized) stabilizer, if any) and thus to the structural rigidity and loss of planarity of the ZnQ_2 complex, which may be the reason behind the superior optical properties and extraordinary stability of QDC in comparison to the ordinary octahedral transplanar ZnQ_2 ·(solvent)₂ complex.

Calculation of ligand density on the surface of ZnS Qdot

Furthermore, the ligand density of HQ on the surface of a Qdot was determined to support the presence of the octahedral ZnQ_2 complex on the surface of the ZnS Qdot or the Z-type binding of HQ to the surface of the ZnS Qdot. This was achieved from the results obtained from (i) NMR spectroscopy – which was used to quantify the ligand (HQ), (ii) transmission electron microscopy (TEM) – which was used for determination of the size of the Qdot and (iii) atomic absorption spectroscopy (AAS) – which was used to obtain total concentration of Zn^{2+} ions present in the dispersion of QDC.^{27,28} The details of calculation have been described in the Experimental section. Notably, the ligand

Scheme 2 Schematic of the projection of zinc quinolato complex on the surface of ZnS Qdot.

density on the surface of ZnS was calculated to be 0.84 nm⁻² (0.42 nm⁻² for 1:2 complex, *i.e.*, ZnQ₂). From reported crystal structure of ZnQ₂·2H₂O, the ligand density of HQ on the ZnS surface was found to be 1.18 nm⁻² (0.56 nm⁻² for ZnQ₂ complex) (considering close packing of ZnQ₂ on the surface of Qdot). The closeness of the ligand density value as obtained from the experimental results and calculation (which is pictorially shown in the Scheme 2) clearly supported the presence of octahedral ZnQ₂ complex (1:2; Z type binding) attached *via* dangling sulphide coordination on the surface of the ZnS Qdot.

Therefore, the Z-type binding mode of HQ is preferred over the X type binding mode when HQ reacted with ZnS to form QDC. Accordingly, QDC has an octahedral ZnQ_2 complex with dangling sulphides in the fifth coordination point and the solvent molecule (which was used during synthesis of QDC) in the sixth coordination point (as is visualized in Scheme 3). Hence, two parallel chemical events are taking place while HQ is getting attached on the surface of the ZnS Qdots. Initially, HQ forms a complex with Zn^{2+} ions originating from the Qdot surface. Then, the complex gets attached on the surface through dangling sulphide ions. Hence, the phenomenon of complexation on the surface is controlled by two parameters – complexation constant of the ligand with the metal ion and adsorption constant of the complex on the surface of the Qdot.

Conclusions

In summary, the presented results indicated that the complexation reaction between ZnS Qdot and HQ lead to the formation of ZnQ₂ on the surface of the Qdot. The dispersibility of the product QDC in polar solvent, solvent-dependent Langmuir model-based binding and density of ligand (otherwise termed as surface coverage) clearly supported the preferable formation of zinc quinolate complex, with a stoichiometry of surface Zn²⁺:HQ as 1:2 (thus to the Z-type binding of HQ) on the surface of the ZnS Qdot. Additionally, ¹H-NMR signals of the desorbed species, which were similar to that of bare octahedral ZnQ₂ complex, clearly supported the aforesaid conclusion. Remarkably, the dangling sulphide accounted for the formation of surface octahedral ZnQ_2 complex and its stability and loss of planarity (in turn gaining structural rigidity) and thus the superior optical features in comparison with those of ordinary ZnQ_2 . This may provide a new idea for understanding the ligand binding chemistry on the surface of Qdots. The products so obtained may find use in light emitting devices, healthcare, energy and in addressing environmental issues.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

We thank the Department of Electronics and Information Technology (No. 5(9)/2012-NANO) (Vol. II), Government of India, for fund. Assistance from CIF, IIT Guwahati, Ayan and Sabyasachi is acknowledged.

Notes and references

- 1 M. A. Boles, D. Ling, T. Hyeon and D. V. Talapin, *Nat. Mater.*, 2016, **15**, 141.
- 2 M. B. Teunis, T. Liyanage, S. Dolai, B. B. Muhoberac, R. Sardar and M. Agarwal, *Chem. Mater.*, 2017, **29**, 8838–8849.
- 3 Y. Cao, A. Stavrinadis, T. Lasanta, D. So and G. Konstantatos, *Nat. Energy*, 2016, **1**, 16035.
- 4 R. Bilan, F. Fleury, I. Nabiev and A. Sukhanova, *Bioconjugate Chem.*, 2015, **26**, 609.
- 5 S.-W. Kim, J. P. Zimmer, S. Ohnishi, J. B. Tracy, J. V. Frangioni and M. G. Bawendi, *J. Am. Chem. Soc.*, 2005, **127**, 10526.
- 6 Y. He, H. Lu, L. Sai, Y. Su, M. Hu, C. Fan, W. Huang and L. Wang, *Adv. Mater.*, 2008, **20**, 3416.
- 7 I. L. Medintz, H. T. Uyeda, E. R. Goldman and H. Mattoussi, *Nat. Mater.*, 2005, **4**, 435.
- 8 P. Zrazhevskiy, M. Sena and X. H. Gao, *Chem. Soc. Rev.*, 2010, **39**, 4326.

- 9 P. Zrazhevskiy and X. Gao, Nano Today, 2009, 4, 414.
- 10 S. Bhandari, S. Roy and A. Chattopadhyay, *RSC Adv.*, 2014, 4, 24217.
- 11 S. Pramanik, S. Bhandari, S. Roy and A. Chattopadhyay, J. Phys. Chem. Lett., 2015, 6, 1270.
- 12 S. Pramanik, S. Bhandari, U. N. Pan, S. Roy and A. Chattopadhyay, *Small*, 2018, 14, 1800323.
- 13 S. Roy, S. Bhandari and A. Chattopadhyay, *J. Phys. Chem. C*, 2015, **119**, 21191.
- 14 S. Roy, M. Manna and A. Chattopadhyay, J. Phys. Chem. C, 2018, 122, 9939.
- 15 M. L. H. Green, J. Organomet. Chem., 1995, 500, 127.
- 16 J. Owen, Science, 2015, 347, 615.
- 17 J. De Roo, K. De Keukeleere, Z. Hens and I. Van Driessche, Dalton Trans., 2016, 45, 13277.
- 18 J. De Roo, Y. Justo, K. D. Keukeleere, F. V. D. Broeck, J. C. Martins, I. V. Driessche and Z. Hens, *Angew. Chem.*, *Int. Ed.*, 2015, 54, 6488.
- 19 N. C. Anderson, M. P. Hendricks, J. J. Choi and J. S. Owen, J. Am. Chem. Soc., 2013, 135, 18536.

- 20 X. Zhou, P. Li, Z. Shi, X. Tang, C. Chen and W. Liu, *Inorg. Chem.*, 2012, **51**, 9226.
- 21 K. A. Grice, G. B. Griffin, P. S. Cao, C. Saucedo, A. H. Niyazi, F. A. Aldakheel, G. E. Sterbinsky and R. J. LeSuer, *J. Phys. Chem. A*, 2018, 122, 2906.
- 22 S. Bhandari, S. Roy, S. Pramanik and A. Chattopadhyay, *Langmuir*, 2014, **30**, 10760.
- 23 R. Koole, P. Schapotschnikow, C. M. Donegá, T. J. H. Vlug and A. Meijerink, *ACS Nano*, 2008, **2**, 1703.
- 24 C. Bullen and P. Mulvaney, Langmuir, 2006, 22, 3007.
- 25 A. J. Morris-Cohen, V. Vasilenko, V. A. Amin, M. G. Reuter and E. A. Weiss, *ACS Nano*, 2012, **6**, 557.
- 26 T. A. Hopkins, K. Meerholz, S. Shaheen, M. L. Anderson, A. Schmidt, B. Kippelen, A. B. Padias, H. K. Hall, N. Peyghambarian and N. R. Armstrong, *Chem. Mater.*, 1996, 8, 344.
- 27 H. Hinterwirth, S. Kappel, T. Waitz, T. Prohaska, W. Lindner and M. Lämmerhofer, ACS Nano, 2013, 7, 1129.
- 28 C. A. Leatherdale, W. K. Woo, F. V. Mikulec and M. G. Bawendi, *J. Phys. Chem. B*, 2002, **106**, 7619.