

Influence of quantum dots on the aromaticity of thiosalicylic acid

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Abstract When ligands are coordinated to quantum dots (QDs), the ring current of the ligand strongly influences the applications of the QDs, for example in solar cell technology. The Raman spectrum of the ligand can be used to probe and identify ions or measure ion concentrations. Here, we investigated, using a theoretical method, the aromaticities and Raman spectra of CdTe, CdSe, and CdS QDs coordinated with thiosalicylic acid ligands. We found that the aromaticity of the benzene ring in free thiosalicylic acid increased when it was used as a QD ligand. The ring currents of the benzene rings in the CdTe–ligand, CdSe–ligand, and CdS–ligand systems were stronger than the ring current of the benzene ring in free thiosalicylic acid; in other words, the QDs influence the ring current—they enhance the electron transfer rate of the benzene ring. We also discovered that the CdTe–ligand and CdSe–ligand systems have stronger ring currents than the CdS–ligand system. The high electronegativity and vacant *d* orbital of the sulfur atom influence the ring current of the ligand in the CdS–ligand system. Further, the Raman spectrum of free thiosalicylic acid was different from the spectra of the ligands in the QD–ligand systems: the Raman spectra of COO[−] in each QD–ligand system was enhanced compared with that of the COO[−] in free thiosalicylic acid.

Keywords Current · Raman spectra · Quantum dots · Ligand

Introduction

QDs have attracted a great deal of attention due to their superior optical properties, such as their broad excitation

spectra, tunable emission, and good photochemical stability. Thus, they have gradually replaced traditional fluorescent dyes in various applications, especially biological applications. QDs are quasi-zero-dimensional nanomaterials about 1–100 nm in size. QDs exhibit obvious quantum size effects [1–3]. Recently, QDs such as CdTe, CdSe, and CdS have been used in solar cells because of their good stability and quantum size effects, as well as the possibility of utilizing their hot electrons to generate multiple electron–hole pairs per photon [4, 5]. Studies of such solar cells have mainly focused on the power conversion efficiency of the solar cell. However, there is still a lack of understanding of the various electron transfer steps associated with these systems [6–10]. Moreover, there have been no theoretical studies of the mechanism of electron transfer.

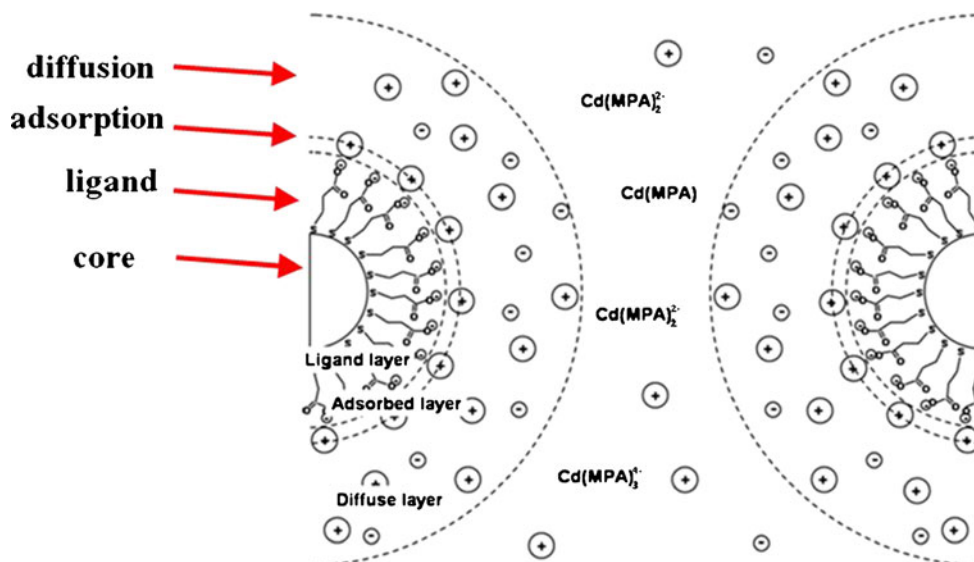
The NICS (nucleus independent chemical shift) value, which is related to the magnetic shielding, has been used to estimate aromaticity, which is an important influence on the stability and ring current of benzene [11–14]. Generally speaking, a negative NICS value denotes aromaticity and good ring current, whereas a positive value shows antiaromaticity and a value of around zero indicates nonaromaticity and a weak ring current.

In addition, Raman spectroscopy is a useful tool for investigating the configuration of a molecule. Since QDs can have various functional groups on their surfaces, Raman spectroscopy can be used to probe the functional groups on QDs and the influence of the QDs on these functional groups.

In this paper, we used NICS values to estimate the aromaticity of the benzene ring in thiosalicylic acid coordinated as a ligand to a QD. We then studied the ring current of the ligand. Contrasting the ring current of free thiosalicylic acid with the ring current of thiosalicylic acid when used as a QD ligand, we found that coordination to a QD enhances the electron transfer rate of the benzene ring. We also investigated the Raman spectra of free thiosalicylic acid and thiosalicylic acid coordinated to a QD.

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Scheme 1 Schematic of the double-layered structure of a QD, taken from [15]



Calculation method

For the DFT (density functional theory) calculations, we adopted Becke's three-parameter hybrid exchange functional with the correlation functional of Lee et al. (B3LYP) as implemented in the Gaussian 03 [16] program. For the molecules HS-C₆H₄-COOH, CdTe, CdSe, and CdS, we chose the LANL2DZ basis set to save computational time. Experimentally, the ligands interact with the QD through Cd atoms on the surface of the core of the QD; see Scheme 1. Therefore, the XCdS-C₆H₄COOH interaction in this molecule is similar to the interaction between the QD and ligand, so it appears reasonable to use the XCdS-C₆H₄-COOH molecule as a model. In addition, Raman spectra were obtained using specific keywords when calculating the frequency, as they could not be created automatically when performing DFT calculations. The NICS values were calculated using a DFT method. NICS values were calculated by NMR-GIAO keyword. In our work, we chose to use water as the solvent in order to simulate aqueous phase synthesis. The dielectric constant of water used in our work was 78.39 ($\epsilon=78.39$).

Results and discussion

Characteristics of thiosalicylic acid (HS-C₆H₄-COOH)

In aqueous solution, and depending on the pH, thiosalicylic acid can adopt one of three forms: ⁻S-C₆H₄-COOH, HS-C₆H₄-COO⁻, or ⁻S-C₆H₄-COO⁻. However, it is also known that the carboxyl moiety is easier to ionize to the anion than to the thiol in aqueous solution, so we can ignore the ⁻S-C₆H₄-COOH form. Experimentally, thiosalicylic acid is not ionized if the pH is lower than 4. When the pH is between 4 and 6, the carboxyl moiety is ionized to COO⁻, leading to the ion HS-C₆H₄-COO⁻. The ⁻S-C₆H₄-COO⁻ form does not exist in aqueous solution unless the pH is higher than 6. Therefore, in this work, we studied the aromaticities of three forms of thiosalicylic acid: HS-C₆H₄-COOH (1); HS-C₆H₄-COO⁻ (2); ⁻S-C₆H₄-COO⁻ (3). The conformations and characteristics of these forms are shown in Fig. 1 and Table 1. Clearly, structures (1) and (3) are planar conformations: their hydrogen, sulfur, oxygen, and carbon atoms are in the same plane. For structure (2), the hydrogen atom bound to the sulfur atom deviates from the plane of benzene. This difference between the conformation of structure (2) and that of the other two structures leads to a higher dipole moment for structure (2): the dipole moments for structures (1), (2), and (3) are 1.1526, 11.5348, and 2.2192 D, respectively. Obviously, the charge of thiosalicylic acid influenced the conformations and the dipole moment.

In order to study the aromaticity, we calculated the NICS values for various locations in the thiosalicylic acid molecule: those of the six carbon atoms of benzene; the NICS value at the center of benzene (σ), and that 1 Å (π) above the benzene ring (Table 1). The NICS values were calculated using a DFT method. We first obtained the optimized configuration and then placed a phantom atom at the center of the benzene. The

Fig. 1 Conformations of the three forms of thiosalicylic acid HS-C₆H₄-COOH, HS-C₆H₄-COO⁻, and ⁻S-C₆H₄-COO⁻

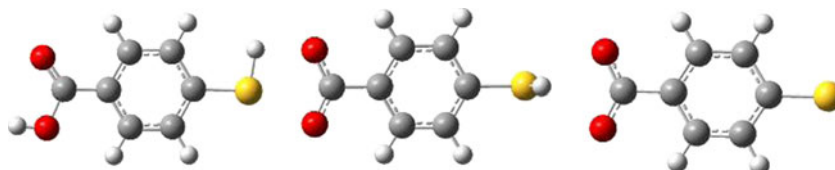
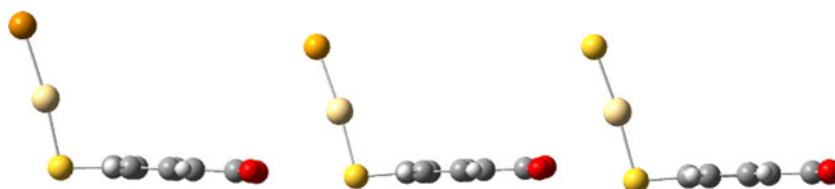


Table 1 NICS values at the center of the benzene ring (“0 Å”), 1 Å above the benzene ring (“1 Å”), and for the six carbons of the benzene ring in HS-C₆H₄-COOH, HS-C₆H₄-COO⁻, and ⁻S-C₆H₄-COO⁻ (“C”)

Form of thiosalicylic acid	NICS values		
	C	0 Å	1 Å
SH-C ₆ H ₄ -COOH	-65, -57, -67, -56, -63, -36	-6.6	-9.0
SH-C ₆ H ₄ -COO ⁻	-58, -58, -44, -58, -58, -60	-7.6	-10.1
⁻ S-C ₆ H ₄ -COO ⁻	-59, -63, -60, -63, -59, -14	-5.5	-8.5

NICS value of the phantom atom at the center of benzene was the NICS value of σ . NICS values were calculated by the NMR-GIAO method. Negative NICS values were obtained at the center and 1 Å above the benzene ring in HS-C₆H₄-COO⁻, showing that it had good aromaticity or a high electron transfer rate. The NICS values of the six carbons in the benzene ring of this structure were similar (-58, -58, -44, -58, -58, -60), showing that electron transfer rate for the benzene ring of the S-C₆H₄-COO⁻ structure was high. However, for the HS-C₆H₄-COOH and ⁻S-C₆H₄-COO⁻ structures, the NICS values of the six carbons in benzene varied significantly. The NICS value of the carbon joined to the sulfur atom in HS-C₆H₄-COOH and ⁻S-C₆H₄-COO⁻ was -36 and -14, respectively. The rather different NICS value of this carbon atom compared to those of the other carbon atoms in the ring indicates that the electron transfer rate of the benzene ring is altered. From the above analysis, we can see that the HS-C₆H₄-COO⁻ structure has the best electron transfer rate. Experimentally, we should therefore use the HS-C₆H₄-COO⁻ structure as the ligand to obtain optimal electron transfer. In fact, the pH of the water solution in such experiments is adjusted to 9.1, which means that the main form of thiosalicylic acid in the water solution is then ⁻S-C₆H₄-COO⁻. From the above discussion, it is clear that this kind of structure does not have the best electron transfer rate. We would get better electron transfer by changing the form of thiosalicylic acid to HS-C₆H₄-COO⁻ during QD synthesis. Considering the pH used experimentally in aqueous QD synthesis, we theoretically investigated the characteristics of CdTe, CdSe, and CdS QDs with ⁻S-C₆H₄-COO⁻ ligands. We also look forward to using HS-C₆H₄-COO⁻ as the ligand in experimental investigations.

Fig. 2 Conformations of the TeCd-S-C₆H₄-COO⁻, SeCd-S-C₆H₄-COO⁻, and SCd-S-C₆H₄-COO⁻ QD-ligand systems**Table 2** NICS values at the center of the benzene ring (“0 Å”), 1 Å above the benzene ring (“1 Å”), and for the six carbons of the benzene ring in the TeCd-S-C₆H₄-COO⁻, SeCd-S-C₆H₄-COO⁻, and SCd-S-C₆H₄-COO⁻ QD-ligand systems

QD-ligand system	NICS values		
	C	0 Å	1 Å
TeCd-S-C ₆ H ₄ -COO ⁻	-54, -57, -64, -65, -56, -66	-11.5	-13.5
SeCd-S-C ₆ H ₄ -COO ⁻	-60, -57, -59, -54, -55, -57	-11.5	-13.1
SCd-S-C ₆ H ₄ -COO ⁻	-53, -55, -49, -54, -51, -22	-0.6	-4.0

Characteristics of the ligand when coordinated to CdTe, CdSe, and CdS QDs

Generally speaking, ligands coordinated to QDs in aqueous solution are in ionic form, for example XCd-S-C₆H₄-COO⁻. We investigated the characteristics of this kind of conformation (Fig. 2). The NICS values of TeCd-S-C₆H₄-COO⁻, SeCd-S-C₆H₄-COO⁻, and SCd-S-C₆H₄-COO⁻ are listed in Table 2. These three structures had the same conformation and showed similar dipole moments (13.5607, 11.9210, and 10.1796 D). The conformation and polarity of the ligand were clearly not influenced by the species of QD, as the X-Cd-S-C₆H₄-COO⁻ structures have the same conformation and polarity. However, TeCd-S-C₆H₄-COO⁻, SeCd-S-C₆H₄-COO⁻, and SCd-S-C₆H₄-COO⁻ have different rates of electron transfer. From the NICS values in Table 2, we can see that TeCd-S-C₆H₄-COO⁻ and SeCd-S-C₆H₄-COO⁻ have similar NICS values at the center of and 1 Å above benzene. Thus, these two structures show similar rates of electron transfer. The NICS values of SCd-S-C₆H₄-COO⁻ were much smaller than those of the other two structures. The wide range of NICS values for the six carbons in benzene also explained the slower electron transfer rate of the SCd-S-C₆H₄-COO⁻ structure. In Table 2, the NICS value of the carbon bound to the sulfur atom is lower than the values for the other five carbon atoms in benzene in the SCd-S-C₆H₄-COO⁻ structure. The different rates of electron transfer shown by these three structures may be caused by their different orbital characteristics. First, the *d* orbitals of Te and Se contain electrons, whereas the *d* orbital of the S atom does not, meaning that it can accept an electron. Therefore, the S atom is more attractive to electrons. Moreover, electrons in the *d* orbitals of Te and Se repulse

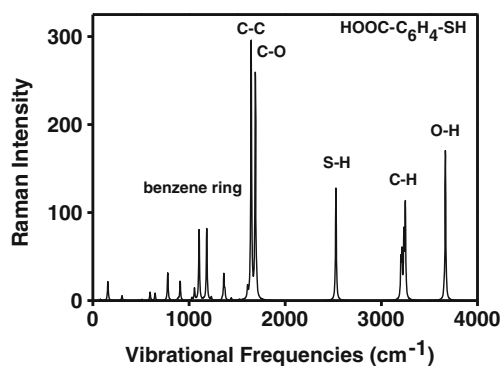


Fig. 3 Raman spectrum of the HOOC-C₆H₄-SH molecule

electrons in the ligand. This is the main reason for the different rates of electron transfer shown by TeCd-S-C₆H₄-COO⁻, SeCd-S-C₆H₄-COO⁻, and SCd-S-C₆H₄-COO⁻. Second, the S atom is more electronegative than the Te and Se atoms. Thus, the S in CdS QDs is more attractive to ligands. Third, the atomic radius of the S atom is smaller than those of the Te and Se atoms. According to the equation $F=kQ_1Q_2/R^2$ (F is the force between two atoms; Q_1 and Q_2 are the charges on the two atoms; R is the distance between the two atoms), it is clear that the S atom should be more attractive than the Te and Se atoms.

Influence of the QD on the Raman spectrum of the ligand

The Raman spectra of HS-C₆H₄-COOH, HS-C₆H₄-COO⁻, and ⁻S-C₆H₄-COO⁻ as well as those of the QD-ligand systems TeCd-S-C₆H₄-COO⁻, SeCd-S-C₆H₄-COO⁻, and SCd-S-C₆H₄-COO⁻ were investigated. The Raman spectra of HS-C₆H₄-COOH, HS-C₆H₄-COO⁻, and ⁻S-C₆H₄-COO⁻ have already been obtained experimentally [17]. We compared those experimental results with the corresponding Raman spectra obtained theoretically in the present study (Fig. 3). For the HS-C₆H₄-COOH structure, we noted features due to the vibrations of S-H, O-H, C-H, and C-C. There was no feature due to the vibration of O-H in the HS-C₆H₄-COO⁻ Raman spectrum, and no features due to O-H and S-H vibrations in the ⁻S-C₆H₄-COO⁻ spectrum. There were also

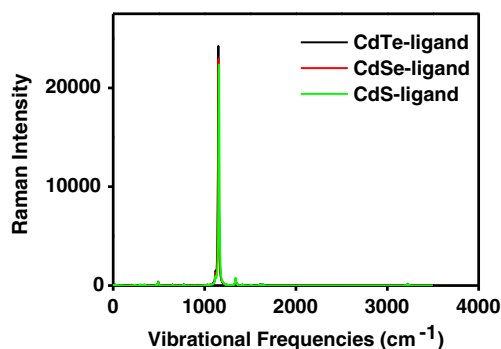


Fig. 4 Raman spectra of the TeCd-S-C₆H₄-COO⁻, SeCd-S-C₆H₄-COO⁻, and SCd-S-C₆H₄-COO⁻ QD-ligand systems

obvious Raman spectral features due to C-H and C-C vibrations in these structures. Although the ⁻S-C₆H₄-COO⁻ spectrum did not show features relating to S-H and O-H, it did show obvious vibrational features for C-C, C-S, and C-H. TeCd-S-C₆H₄-COO⁻, SeCd-S-C₆H₄-COO⁻, and SCd-S-C₆H₄-COO⁻ (Fig. 4) presented completely different Raman spectra to those of the above three structures. For the QD-ligand systems, but not the free ligand structures, there was a very strong vibrational feature at 1,147 cm⁻¹ relating to C-C bonding between the carbon atom of benzene and the carbon atom of the carboxyl moiety. Thus, the coordination of CdTe, CdSe, or CdS to the ligand structures enhanced this C-C vibration. It also made COO⁻ more active, facilitating the binding of COO⁻ to other ions or groups. Thus, we can speculate that coordinating the QDs to ⁻S-C₆H₄-COO⁻ ligands makes it easier for the ligands to bond with other ions.

Conclusions

The ring current of the benzene ring in various thiosalicylic acid structures coordinated as ligands to CdTe, CdSe, and CdS quantum dots (QDs) has been investigated theoretically at the DFT/B3LYP level using the LanL2DZ basis set. The NICS values of three thiosalicylic acid ligand structures were calculated. We found that the CdTe-ligand, CdSe-ligand, and CdS-ligand systems showed stronger ring currents than that of free thiosalicylic acid. Thus, coordination to QDs enhanced the ring current of benzene in the thiosalicylic acid structures. We also discovered that the CdS-ligand systems had different levels of ring current than the CdTe-ligand and CdSe-ligand systems. The ring currents in the CdS-ligand systems were influenced by the vacant d orbital and the high electronegativity of the S atom. The Raman spectrum of thiosalicylic acid changes when it coordinates with a QD. The Raman spectral features due to COO⁻ in the QD ligands are enhanced compared with those seen for the free thiosalicylic acid structures. Therefore, it is possible to probe the characteristics of QD-ligand systems by monitoring the changes that occur to the Raman spectrum of the ligand upon coordination to the QD.

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