

REGULAR ARTICLE

# Theoretical study on the molecular structure, intermolecular interaction and spectral features of 2-aminopyridine/2,3-dichloro-5,6-dicyano-1,4-benzoquinone complex

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**Abstract.** Density function theory (DFT) was performed to study the structures and binding energies of the 2-aminopyridine(2-AP)/2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) complex. Four distinct stable conformers (denoted as **S1–S4**) were located and the bonding characteristics of these conformers were investigated with NBO and AIM analysis. It was revealed that **S1** is formed by the edge(2-AP)-to-face(DDQ) linkage, which is stabilized by a moderate  $\sigma$ - $\pi$  interaction and hydrogen bonding interaction. **S2** and **S3** are formed by the face(2-AP)-to-face(DDQ) linkage through  $\sigma$ - $\pi$  and  $\pi$ - $\pi$  interactions, and **S4** is constructed by the edge(2-AP)-to-edge(DDQ) linkage through halogen bonding and hydrogen bonding interactions. The electronic excitation energies of the two stable conformers, **S2** and **S3**, were calculated with time-dependent DFT (TDDFT), which revealed that the 2-AP( $\pi$ )  $\rightarrow$  DDQ( $\pi^*$ ) charge transfer transitions in conformers **S2** and **S3** contribute to the two new charge transfer absorption bands which were experimentally observed at 598 nm and 557 nm for the 2-AP/DDQ complex in chloroform.

**Keywords.** Density functional theory; 2-AP/DDQ complex; NBO; AIM.

## 1. Introduction

Charge transfer (CT) complexes originating from intermolecular interactions between electron donors and accepters have been extensively investigated due to their various applications in organic electronics, optical devices and organic synthesis.<sup>1–3</sup> A thorough understanding of the intermolecular interactions between the electron donor and acceptor is of considerable fundamental and practical interest. Nitrogen-containing aromatic heterocyclic compounds can function as  $n$  and  $\pi$  type of electron donors to form charge transfer complexes with different electron accepters.<sup>4–9</sup> Among them, aminopyridine (AP) compounds are of special interest because of their significant roles in both biological and chemical processes. 2-AP dimer can be considered as a mimetic model to study the light-induced single and double proton transfer processes of Watson–Crick DNA base pairs.<sup>10</sup> 2-AP/2-pyridone complex linked through antiparallel N–H  $\cdots$  O = C and N–H  $\cdots$  N hydrogen bonds provided a model for the Watson–Crick hydrogen bonding configuration of the adenine–thymine and adenine–uracil nucleobase pairs.<sup>11</sup> Moreover, AP as an analytical reagent

has many uses in analytical chemistry. It has been recognized that quinone compounds play a vital role in the biological electron transport processes such as photosystems I and II of photosynthesis and aerobic respiration.<sup>12</sup> 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) is a well-known member of the quinone family, and its charge transfer complexes formed with many electron donors present novel optical and electronic properties.<sup>13,14</sup> In the past few years, several kinds of charge transfer complexes formed by AP donors and DDQ accepters have been prepared and characterized by UV–Vis and infrared spectra. The stoichiometries and the formation constants of the studied complexes were determined from photometric titration methods.<sup>7–9</sup>

However, the basic issues of the AP/DDQ complex, such as the preferable geometry, the bonding characteristics, and the nature of the observed new absorption bands, have not been well understood. Therefore, in the present article, we report our experimental and theoretical results of the 2-AP/DDQ complex. The preferable geometries and binding energies of the complex were studied using density functional theory (DFT). Natural bond orbital analysis and topological analysis of electron densities were employed to explore the nature and the strength of the intermolecular interactions. In

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addition, the electronic excited states were calculated with time-dependent density function theory (TDDFT) to provide a deeper understanding of the observed UV-Vis absorption spectrum of the 2-AP/DDQ complex.

## 2. Computational

The molecular structures and binding energies of 2-AP/DDQ complex in the ground states were calculated with M06-2x-D3 method,<sup>15</sup> which has been applied to study a number of intermolecular interactions successfully.<sup>16–18</sup> Vibrational frequency computations for the optimized structures were done to confirm the optimized structure to be an energy minimum and to evaluate the zero point energy (ZPE). The 6–31 + G(d) basis set was used in the structure optimizations and frequency calculations. Boys and Bernardi's counterpoise (CP) method was applied to correct the basis set superposition errors (BSSEs).<sup>19</sup> In order to estimate the influence of the basis set on the binding energy, the interaction energies were calculated with larger basis sets at the optimized geometry.

Charge transfer from 2-AP to DDQ was estimated using natural population analysis (NPA). Natural bond orbital (NBO) analysis and Bader's atoms-in-molecule (AIM) analysis were performed to explore the nature and strength of intermolecular interactions between 2-AP and DDQ in the complex.<sup>20,21</sup> The electronic excitation energies and oscillator strengths of the 2-AP/DDQ complex were calculated with time-dependent density functional theory (TDDFT) using PBE1PBE methods with 6–311G(d,p) basis set, and solvation effect (chloroform) was considered by using the integral equation formalism polarisable continuum model (IEFPCM).<sup>22,23</sup> All DFT calculations were performed using Gaussian 09 program.<sup>24</sup>

## 3. Results and Discussion

### 3.1 Structural geometry and binding energy

The possible conformations of the 2-AP/DDQ complex was fully optimized in gas phase without any symmetry constraints using M06-2x-D3/6–31+G(d) method. The stoichiometry of 2-AP and DDQ is 1:1 which is adopted from the literature.<sup>9</sup> Four distinct stable conformers, denoted as **S1**, **S2**, **S3** and **S4**, were obtained and these are displayed in Figure 1. Vibrational frequencies were calculated based on the optimized geometries and absence of negative frequencies confirmed that the four conformers were local minimum-energy structures.

As shown in Figure 1, **S1** has a slightly inclined T-shape structure with 2-AP perpendicular to the mean plane of DDQ ring. DDQ displays slightly nonlinear distortion with O<sub>8</sub> away from 2-AP. The distance between C<sub>3</sub> and N<sub>17</sub> is 2.67 Å, which is much shorter than the

sum of the van der Waals radii of C and N atoms (3.25 Å)<sup>25</sup> and shows that it exists a moderately strong attractive interaction between the two atoms. In addition, the O<sub>8</sub>...H<sub>26</sub> distance (2.15 Å) is significantly shorter than the sum of the van der Waals radii of O and H atoms (2.72 Å),<sup>25</sup> which indicates a rather strong hydrogen bonding interaction between DDQ and 2-AP. For **S2** and **S3**, the positions of 2-AP and DDQ present parallel-displaced orientations. The vertical and horizontal displacements are 3.02 Å and 1.85 Å for **S2** and 3.03 Å and 1.82 Å for **S3**, respectively. These distances are compatible with the typical stacking interaction. The positions of 2-AP and DDQ of conformer **S4** are nearly in the same plane. The distance (2.93 Å) between N<sub>17</sub> and Cl<sub>10</sub>, which is slightly shorter than the sum of the van der Waals radii of Cl and N atoms (3.30 Å),<sup>25</sup> indicates that there is moderately strong halogen bonding between the two atoms. In addition, the distances of O<sub>8</sub>...H<sub>26</sub> and Cl<sub>10</sub>...H<sub>26</sub> are 2.47 Å and 2.66 Å, respectively, which are nearly close to the sum of the van der Waals radii of O and H atoms (2.72 Å) and Cl and H atoms (2.81 Å),<sup>25</sup> and weak hydrogen bonding interactions between 2-AP and DDQ seem to exist.

In order to estimate the influence of basis set on the binding energy, the binding energies of **S1–S4** were calculated using 6–31++G(d,p) and 6–311G(d,p) basis sets at the M06-2X-D3/6–31+G(d) optimized geometries through counterpoise (CP) and zero point energy (ZPE) corrections. The calculated results are tabulated in Table 1. It is shown that the binding energies of **S1–S4** calculated with 6–31++G(d,p) and 6–311G(d,p) basis sets are compatible with those calculated with 6–31+G(d) basis set, which indicates that a moderate basis set, 6–31+G(d), could be used in the calculation of the binding energy.

### 3.2 NPA and NBO analysis

Charge transfer from the donor (2-AP) to the acceptor (DDQ) was estimated using NPA with M06-2X-D3/6–311G(d,p) method. The results revealed that there is a positive charge on the 2-AP part of **S1–S4** (0.0718e, 0.1117e, 0.1183e, and 0.0080e, respectively) whereas an equivalent negative charge is on the DDQ unit. The charge distributions indicate a net charge flow from the donor of 2-AP to the acceptor of DDQ.

To better understand the intermolecular interaction of the 2-AP/DDQ complex, NBO analysis has been carried out with M06-2X-D3/6–311G(d,p) method, which provides much information about the nature and strength of intermolecular interactions from the viewpoint of local orbital interactions and their second order perturbation energy ( $E^{(2)}$ ).<sup>20</sup> Table 2 lists the  $E^{(2)}$  values of selected



**Table 2.** The selected local orbital interactions and their  $E^{(2)}$  values of **S1–S4** (threshold: 0.5 kcal/mol).

Conformer	Donor NBO(i)	Acceptor NBO(j)	$E^{(2)}$ (kcal/mol)
<b>S1</b>	BD( $\pi$ )C <sub>3</sub> –O <sub>8</sub>	BD*( $\sigma$ )N <sub>21</sub> –H <sub>26</sub>	1.02
	LP( $\sigma$ )O <sub>8</sub>	BD*( $\sigma$ )N <sub>21</sub> –H <sub>26</sub>	0.82
	BD( $\pi$ )N <sub>17</sub> –C <sub>18</sub>	BD*( $\pi$ )C <sub>3</sub> –O <sub>8</sub>	0.76
	LP( $\sigma$ )N <sub>17</sub>	BD*( $\pi$ )C <sub>1</sub> –C <sub>2</sub>	3.06
	LP( $\sigma$ )N <sub>17</sub>	BD*( $\pi$ )C <sub>3</sub> –O <sub>8</sub>	5.97
<b>S2</b>	BD( $\pi$ )N <sub>17</sub> –C <sub>18</sub>	BD*( $\pi$ )C <sub>1</sub> –C <sub>2</sub>	1.31
	BD( $\pi$ )N <sub>17</sub> –C <sub>18</sub>	BD*( $\pi$ )C <sub>3</sub> –O <sub>8</sub>	1.11
	LP( $\sigma$ )N <sub>21</sub>	BD*( $\pi$ )C <sub>1</sub> –C <sub>2</sub>	1.36
	LP( $\sigma$ )N <sub>21</sub>	BD*( $\pi$ )C <sub>6</sub> –O <sub>7</sub>	4.25
<b>S3</b>	BD( $\pi$ )N <sub>17</sub> –C <sub>18</sub>	BD*( $\pi$ )C <sub>3</sub> –O <sub>8</sub>	1.23
	BD( $\pi$ )N <sub>17</sub> –C <sub>18</sub>	BD*( $\pi$ )C <sub>4</sub> –C <sub>5</sub>	0.77
	BD( $\pi$ )C <sub>19</sub> –C <sub>20</sub>	BD*( $\pi$ )C <sub>1</sub> –C <sub>2</sub>	0.91
	LP( $\sigma$ )N <sub>21</sub>	BD*( $\pi$ )C <sub>1</sub> –C <sub>2</sub>	1.59
	LP( $\sigma$ )N <sub>21</sub>	BD*( $\pi$ )C <sub>6</sub> –O <sub>7</sub>	4.21
<b>S4</b>	LP( $\pi$ )O <sub>8</sub>	BD*( $\sigma$ )N <sub>21</sub> –H <sub>26</sub>	0.76
	LP( $\pi$ )Cl <sub>10</sub>	BD*( $\sigma$ )N <sub>21</sub> –H <sub>26</sub>	1.09
	LP( $\sigma$ )N <sub>17</sub>	BD*( $\sigma$ )C <sub>4</sub> –Cl <sub>10</sub>	2.95

ing orbital of 2-AP and antibonding orbital of DDQ, and these interactions are characterized by BD( $\pi$ )N<sub>17</sub>–C<sub>18</sub>  $\rightarrow$  BD\*( $\pi$ )C<sub>1</sub>–C<sub>2</sub>/BD\*( $\pi$ )C<sub>3</sub>–O<sub>8</sub> for **S2**, BD( $\pi$ )N<sub>17</sub>–C<sub>18</sub>  $\rightarrow$  BD\*( $\pi$ )C<sub>3</sub>–O<sub>8</sub> and BD( $\pi$ )C<sub>19</sub>–C<sub>20</sub>  $\rightarrow$  BD\*( $\pi$ )C<sub>1</sub>–C<sub>2</sub> for **S3**, respectively. As indicated in Table 2, the main interactions of **S4** turn out to be halogen bonding and hydrogen bonding interactions, which are characterized by LP( $\sigma$ )N<sub>17</sub>  $\rightarrow$  BD\*( $\sigma$ )C<sub>4</sub>–Cl<sub>10</sub> and LP( $\pi$ )Cl<sub>10</sub>/LP( $\pi$ )O<sub>8</sub>  $\rightarrow$  BD\*( $\sigma$ )N<sub>21</sub>–H<sub>26</sub>, and the corresponding  $E^{(2)}$  values are 2.95 kcal/mol, 0.76 kcal/mol and 1.09 kcal/mol, respectively.

### 3.3 AIM analysis

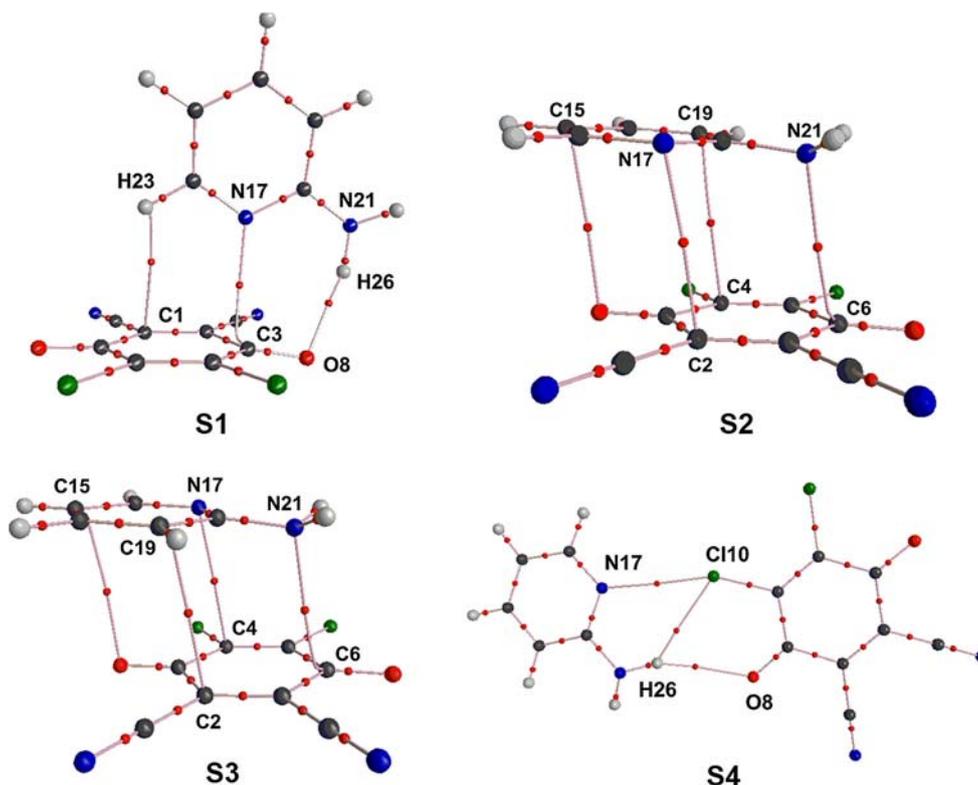
It is well known that Bader's topological analysis of charge density  $\rho(r)$  could be widely employed to investigate the intermolecular interactions.<sup>26–30</sup> In this approach, the location of bond critical point (BCP), the value of charge density  $\rho(r)$  and its Laplacian charge density  $\nabla^2\rho(r)$  at the BCP provide vital information of the nature and strength of the interactions in the formation of complexes. The intermolecular interactions between 2-AP and DDQ in **S1–S4**, identified *via* AIM analysis are shown in Figure 2. The values of charge densities and their Laplacians at the BCPs are tabulated in Table 3.

As shown in Figure 2 and Table 3, there are three intermolecular BCPs in **S1**; one in the path joining C<sub>3</sub> and N<sub>17</sub> and the other two in the path joining O<sub>8</sub> and H<sub>26</sub>, and C<sub>1</sub> and H<sub>23</sub>. At the BCP between C<sub>3</sub> and N<sub>17</sub>, the charge density  $\rho(r)$  and its Laplacian

$\nabla^2\rho(r)$  are 0.0193 a.u. and 0.0646 a.u., respectively. The O<sub>8</sub>  $\cdots$  H<sub>26</sub> and C<sub>1</sub>  $\cdots$  H<sub>23</sub> BCPs hint the existence of weak hydrogen bonds between O<sub>8</sub> and H<sub>26</sub> (or C<sub>1</sub> and H<sub>23</sub>). The presence of four BCPs in the stacking region of **S2** and **S3** reveal that there exist intermolecular interactions between 2-AP and DDQ. As indicated in Table 3, The charge densities  $\rho(r)$  at the four BCPs range from 0.0070 a.u. to 0.0150 a.u., and their Laplacian  $\nabla^2\rho(r)$  are in the range of 0.0230 a.u. to 0.0480 a.u.. As displayed in Figure 2, all the topographical features in **S2** and **S3** are similar. The intermolecular dispersion plays a considerable role in the stabilization of the two complexes in addition to the electrostatic interaction. The BCP located between N<sub>17</sub> and Cl<sub>10</sub> of **S4** indicates the existence of halogen bonding interaction between N<sub>17</sub> and Cl<sub>10</sub>. The O<sub>8</sub>  $\cdots$  H<sub>26</sub> and Cl<sub>10</sub>  $\cdots$  H<sub>26</sub> BCPs reveal that there exist two different hydrogen bonding interaction in **S4**. As shown in Table 3, all the charge densities at the BCPs are relatively small, and their Laplacian are positive; it indicates that the intermolecular interactions are typical close-shell interactions. All the AIM analysis results are in agreement with those of NBO analysis.

### 3.4 UV–Vis absorption spectra and TDDFT calculation

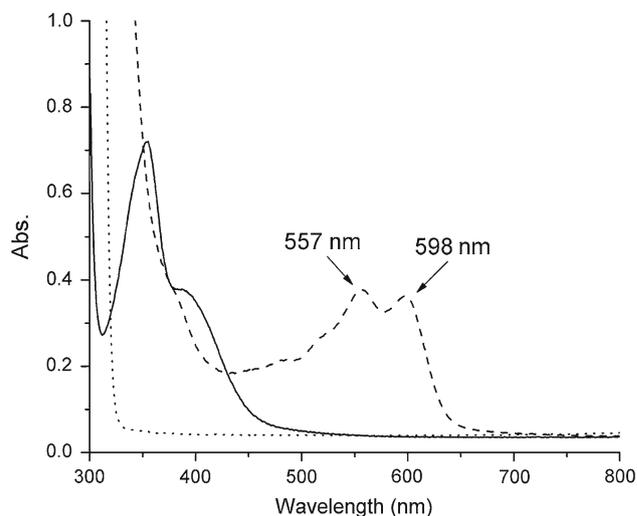
Analytical grade 2-AP and DDQ were used without further purification. The solutions of 2-AP and DDQ were prepared in chloroform, and the corresponding concentrations are 7.56 mmol/L and 0.73 mmol/L, respectively. The solutions of 2-AP and DDQ were mixed at the same



**Figure 2.** Charge density topography features of **S1–S4** (ring critical points (RCPs) and cage critical points (CCPs) are omitted).

**Table 3.** The charge densities (a.u.) and their Laplacians (a.u.) at the intermolecular BCPs of **S1–S4** calculated with M06-2X-D3/6–311G(d,p) method.

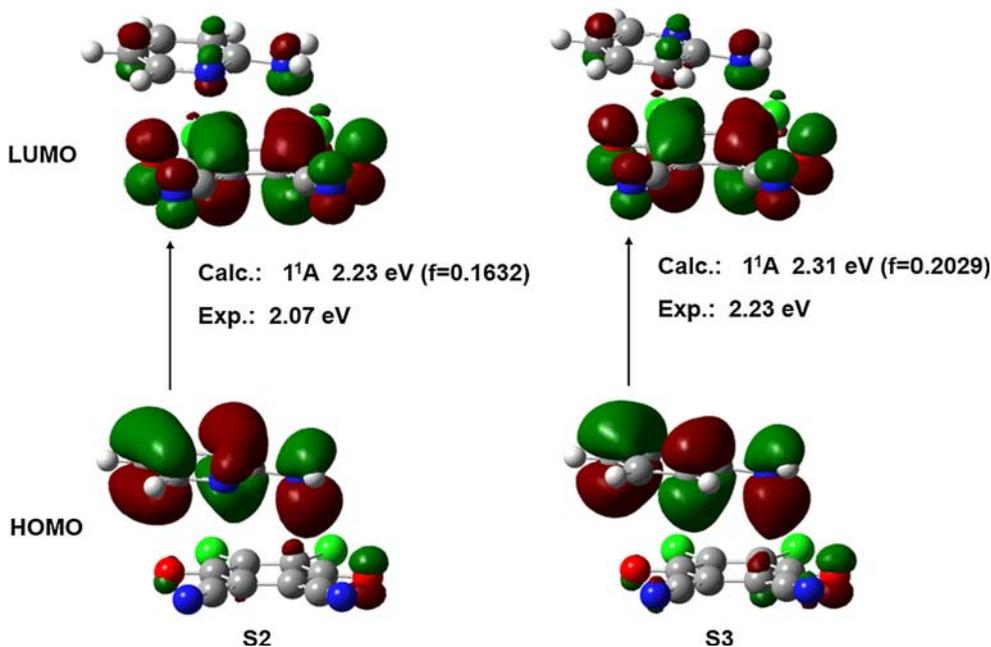
Conformer	BCPs	$\rho(r)$	$\nabla^2\rho(r)$
<b>S1</b>	C1...H23	0.0070	0.0211
	C3...N17	0.0193	0.0646
	O8...H26	0.0144	0.0731
<b>S2</b>	C2...N17	0.0121	0.0385
	C4...C19	0.0099	0.0282
	C6...N21	0.0147	0.0473
<b>S3</b>	O8...C15	0.0080	0.0243
	C2...C19	0.0113	0.0322
	C4...N17	0.0103	0.0319
<b>S4</b>	C6...N21	0.0148	0.0473
	O8...C15	0.0078	0.0233
	O8...H26	0.0077	0.0271
	C10...H26	0.0085	0.0320
	C10...N17	0.0152	0.0531



**Figure 3.** UV-Vis absorption spectra of 2-AP (dot), DDQ (solid) and the 2-AP/DDQ complex (dash) in chloroform

volume, and the concentrations of 2-AP and DDQ in the mixture are 3.78 mmol/L and 0.365 mmol/L, respectively. UV-Vis absorption spectra of the molecules and the mixture were measured after 30 min using a quartz cell of 0.5 cm light path, and the spectral slit width

was 2 nm. As displayed in Figure 3, compared with the absorption of the individual molecules, there are two new absorption bands at 557 nm and 598 nm, which are assigned to the charge transfer absorption of the 2-AP/DDQ complex.



**Figure 4.** The calculated frontier molecular orbitals, excitation energies ( $\Delta E$  in eV) and oscillator strengths ( $f$ ) of **S2** (left) and **S3** (right); the experimental data were obtained from the solution spectrum in chloroform.

In order to elucidate the nature of the observed UV-Vis absorption of 2-AP/DDQ complex, particularly, the two new charge transfer absorption bands, the excitation energies from  $S_0$  to  $S_{30}$  states of the more stable conformers (*i.e.*, **S2** and **S3**) were calculated using TDDFT with PBE1PBE/6-311G(d,p) methods based on the optimized ground state geometries, because the energy needed for the isomerization of the two conformers is only about 1.00 kJ/mol. For simplicity, only the first lowest energy transition, namely  $S_0$  to  $S_1$  is discussed here. The solvent was chloroform in which the UV-Vis spectroscopy of the complex was performed. The calculated frontier molecular orbitals, excitation energies and oscillator strengths ( $f$ ) in chloroform are displayed in Figure 4.

As shown in Figure 4, the calculated excitation energies of the first excited singlet states (from  $S_0$  to  $S_1$ ) are 2.23 eV and 2.31 eV for **S2** and **S3**, respectively, which are closer to the two new absorption bands (2.07 eV and 2.23 eV) observed experimentally. As a result, it indicates that for the studied system, PBE1PBE method gives better excited state properties in comparison with the experimental data. As shown in Figure 4, The HOMOs and the LUMOs of **S2** and **S3** are almost constructed by the HOMO of 2-AP and the LUMO of DDQ, which are the 2-AP( $\pi$ )  $\rightarrow$  DDQ( $\pi^*$ ) charge transfer transitions in character. Hence, we attribute the calculated first excited singlet states of **S2** and **S3** to the

two new charge transfer absorption bands observed at 598 nm (2.07 eV) and 557 nm (2.23 eV) in Figure 3, respectively.

#### 4. Conclusions

In summary, the probable structures and their binding energies of the 2-AP/DDQ complex have been studied using density functional theory. The calculated results located four different stable conformers (denoted as **S1-S4**), and **S2** is more stable than the other conformers. Natural population analysis indicated a net charge transfer from 2-AP to DDQ. Natural bond orbital and atoms-in-molecule analysis revealed that **S1** is formed by the edge(2-AP)-to-face(DDQ) linkage, which is considered in favor of  $\sigma$ - $\pi$  and hydrogen binding interactions. **S2** and **S3** are formed by the face(2-AP)-to-face(DDQ) linkage through  $\sigma$ - $\pi$  and  $\pi$ - $\pi$  interactions. **S4** is constructed by the edge(2-AP)-to-edge(DDQ) linkage through halogen bonding and hydrogen bonding interactions. UV-Vis absorption spectra of 2-AP, DDQ and the 2-AP/DDQ complex were recorded in chloroform. Compared with the absorption spectra of 2-AP and DDQ, two new absorption bands at 557 nm and 598 nm were observed in 2-AP/DDQ complex, which are attributed to the charge transfer absorption of the 2-AP/DDQ complex. The

electronic excitations of the 2-AP/DDQ complex (**S2** and **S3**) were calculated with TDDFT, which revealed that the 2-AP( $\pi$ )  $\rightarrow$  DDQ( $\pi^*$ ) charge transfer transitions in conformers **S2** and **S3** are responsible for the two new charge transfer absorption bands of the 2-AP/DDQ complex.

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