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Experimental and theoretical studies on the photoinduced acute toxicity of a series of anthraquinone derivatives towards the water flea (*Daphnia magna*)

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ABSTRACT

The photoinduced acute toxicity of fourteen anthraquinone derivatives to *Daphnia magna* was investigated. Whilst in the dark, all of dyes exhibited no observable toxicity at the maximum test concentration used, in the presence of visible light, all of the colorants, with the exception of three nitroanthraquinones, were acutely toxic towards the water flea over a wide range of medium effective concentrations (4.3–4186.7 nmol L^{-1}). Generally, the acute toxicity of the dyes was higher in the presence of full-spectrum simulated solar radiation compared with visible light; in addition, the photoinduced toxicity of the dyes increased with increase in their hydrophobicity. The energy gap between the lowest unoccupied molecular orbital and the highest occupied molecular orbital was found to indicate the relative photoinduced toxicity of the dyes. Time-dependent density functional theory calculations revealed that singlet oxygen and the superoxide anion could be generated through direct energy transfer or autoionization of the excited state of the dyes.

1. Introduction

Some organic chemicals such as polycyclic aromatic compounds exert photoinduced toxicity to numerous aquatic species in the presence of solar radiation [1,2]. The mechanism of photoinduced toxicity can be generally classified as photosensitization associated with generation of reactive oxygen species (ROS) and photomodification to more toxic photoproducts [3–7]. The photoinduced toxicity of polycyclic aromatic hydrocarbons (PAHs) has been well documented [8–12]; however, little information is available concerning other potential contaminants.

Anthraquinone derivatives (AQs) are a group of important chemicals used in dye, pharmaceutical and pulp industries. AQ dyes are commonly used in the textile industry and some are acutely toxic, mutagenic and carcinogenic [13–18]. Nearly 12% of the dyes used yearly are lost during dyestuff manufacturing and textile dyeing operations, and 20% of these losses are discharged into the environment [19]. The environmental photoinduced toxicity of AQ dyes to aquatic organisms potentially exists due to their absorption of visible light and UV light. Previous experimental studies indicated that biological damaging ROS could be generated through the photosensitization reactions of some AQs in solutions [20,21]. Thus it is of interest to further investigate the phototoxic pathway of AQs.

The objective of this study was to evaluate the photoinduced acute toxicity of 14 AQs through experiments and quantum chemical calculations. Acute toxicity of 14 AQs to *Daphnia magna*, an aquatic invertebrate commonly used for regulatory toxicity testing, was determined in the presence/absence of light. Then energy gap (E_{GAP}) between the energy of the lowest unoccupied molecular orbital (E_{LUMO}) and the highest occupied molecular orbital (E_{HOMO}) was adopted to assess the photoinduced toxicity. To better understand the photosensitization pathway of the AQs, the theoretical calculations were performed using time-dependent density functional theory (TD-DFT).

2. Experimental

2.1. Test chemicals

Fourteen AQs with substituents $-NH_2$, –Cl, –Br, $-NO_2$, $-SO_3H$ or –OH were obtained from the State Key Laboratory of Fine Chemicals (Dalian University of Technology) and Sinochem Liaoning Imp. & Exp. Corp. Their purities were given in Table 1. They were

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Table 1
Physicochemical properties and purities of 14 anthraquinone derivatives used in this study.

No.	Compound	Purity (%)	log K_{OW}	E_{GAP}[a] (eV)	λ_{max}[b] (nm)
1	1-Amino-2,4-dibromoanthraquinone	98.4	5.31	7.486	479
2	1-Amino-2-methyl-4-bromoanthraquinone	99.2	4.96	7.490	485
3	1-Amino-2-bromoanthraquinone	95.5	4.42	7.498	473
4	1,8-Dichloroanthraquinone	98.9	4.63	8.277	339
5	1,5-Diaminoanthraquinone	95.1	3.71	7.466	492
6	1-Chloroanthraquinone	99.0	3.99	8.313	337
7	1,8-Dihydroxyanthraquinone	96.2	3.94	7.991	428
8	1-Amino-4-bromoanthraquinone	95.8	4.42	7.532	482
9	1-Aminoanthraquinone	98.3	3.53	7.732	482
10	1-Amino-4-bromoanthraquinone-2-sulfonic acid	95.3	1.26	7.318	490
11	1,2-Dihydroxyanthraquinone	95.7	3.16	8.200	435
12	1-Nitroanthraquinone	99.3	3.16	8.782	325
13	1,8-Dinitroanthraquinone	97.6	2.98	9.029	321
14	1,5-Dinitroanthraquinone	96.3	2.98	9.080	325

[a] E_{GAP} is the energy gap between energy of the lowest unoccupied molecular orbital (E_{LUMO}) and the highest occupied molecular orbital (E_{HOMO}).
[b] λ_{max} is the maximum of absorbance wavelength (290–600 nm) of anthraquinone derivatives at 125 μmol/L in DMSO.

dissolved in dimethyl sulfoxide (DMSO) to make primary stock solutions. The final concentration of DMSO in the test solutions was a constant of 0.1% and control experiments carried out with equivalent volumes of DMSO exhibited no acute toxicity on *D. magna*.

2.2. Toxicity assays

D. magna were cultured under cool-white fluorescent light (FSL, YZ36RR26, 40 W) with a 14 h light/10 h dark photoperiod. The temperature of the test chamber was maintained at 20 ± 1 °C. Culture water was prepared by non-chlorinated tap water saturated with dissolved oxygen. *Scenedesmus obliquus* were fed to *D. magna* daily. The acute toxicity assay with neonates (<24 h old) of *D. magna* was performed in all the bioassays. The toxicological endpoint was the immobilization after 24 h-exposure to the chemicals. Each treatment was performed in triplicate, with 10 animals per replicate in Pyrex beakers containing 50 mL of the test solution. The daphnids were considered to be immobile if they were not able to swim within 15 s of observation after gentle agitation of the test container. All the experiments were repeated independently at least three times. Medium effective concentration (EC_{50}) values with 95% confidence limits were calculated using Probit analysis (US EPA, 1993). Values presented as means were obtained from a minimum of three independent replicates.

2.3. Light conditions

Three different light sources, including visible light, visible light plus UV-A and simulated solar radiation (SSR; consisting of visible light plus UV-A and UV-B), were adopted in this study. The full-spectrum SSR included four visible light tubes, two UVA-365 tubes and one UVB-313 tube [22]. The spectral output of SSR (Fig. 1) was determined by a monochromator (Acton, SP-300i, USA, 200 nm–800 nm). Two different photoperiods, 14:10 h light:dark for visible light and UV-A, and 3:21 h light:dark for UV-B, were chosen. The irradiance of SSR was 307.8 ± 67.7 μW/cm^2 for visible light, 74.4 ± 31.6 μW/cm^2 for UV-A and 8.4 ± 5.4 μW/cm^2 for UV-B.

2.4. Chemical analysis

To investigate the photostability of the AQs, 50 mL of the AQ solutions were placed inside of the Pyrex tubes under visible light or in the dark for 48 h. The nominal concentration of AQs in culture medium was 10 μM except 1-amino-2,4-dibromoanthraquinone (2.5 μM) and 1-amino-2-methyl-4-bromoanthraquinone (5 μM). The sample solutions except water soluble 1-amino-4-bromo anthraquinone-2-sulfonic acid were extracted three times with dichloromethane. The extracts were combined and concentrated by a rotary evaporator. The final traces of dichloromethane were removed under a stream of nitrogen and the solvent was replaced by acetonitrile. Then the UV–visible absorption spectra were recorded by Hitachi UV2800 spectrophotometer.

3. Computational software and methods

E_{HOMO} and E_{LUMO} were derived by the semiempirical PM3 Hamiltonian of MOPAC 2000 contained in the CS Chem3D Ultra software (Version 8.0, CambridgeSoft, Cambridge, UK). The computational process was adopted as follows. Draw the molecular structures in Chem3D and the energy minimizing was selected from the MOPAC menu and run. When the optimization was completed, E_{HOMO} and E_{LUMO} were obtained from the output files. The logarithm values of the octanol/water partition coefficients (logK_{OW}) of AQs were estimated by KOWWIN v1.67 (EPI Suite, U.S. EPA) using SMILES code as input.

For the Gaussian 03 computation [23], the initial geometries of AQs, their neutral molecules, radical anions and radical cations of the AQs were preoptimized by PM3 Hamiltonian. Then the created GJF files were employed as the input files for the Gaussian 03

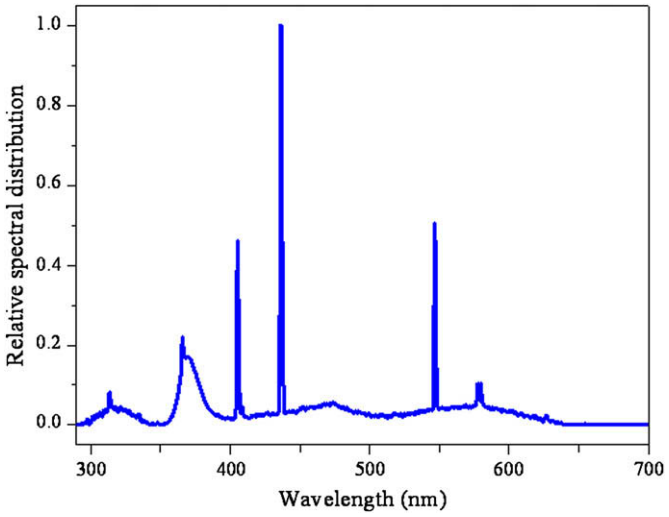

Fig. 1. Spectral output (given in relative units on photon fluence rate) of simulated solar radiation.

program and the geometries of the AQs were optimized at the B3LYP/6-31G(d,p) level of theory. Frequency calculations were performed on the optimized geometries to ascertain the stationary points. The excited energy was calculated using TD-DFT. Single point and the excited energy calculations were performed at B3LYP/6-31+G(d,p) level. The solvent effects were taken into consideration by employing the self-consistent reaction field method (SCRF) with the integral equation of the polarized continuum model (IEFPCM) and water was used as the solvent. The energy optimization of 1-amino-4-bromoanthraquinone-2-sulfonic acid was determined in vacuum, but its optimization in water was not completed because the maximum force and RMS force were not converged. Thus, 1-amino-4-bromoanthraquinone-2-sulfonic acid was not selected for calculations.

4. Results and discussion

4.1. Photoinduced acute toxicity of 14 AQs to D. magna

In the dark, 14 tested AQs exhibited no observable acute toxicity to *D. magna* at the maximum test concentration available. Under visible light, three nitro-substituted AQs were non-phototoxic; in comparison, the other 11 AQs were acutely toxic to *D. magna* with a wide range of EC_{50} values from 4.3 nmol/L to 4186.7 nmol/L (Table 2). The AQs showed a toxicity increase in the range of $EC_{50(dark)}/EC_{50(visible\ light)}$ from 1.2 to 581.4 which was rationalized by the well-known strong absorbance of AQs in the visible spectral region. One compound, 1-amino-2,4-dibromoanthraquinone, which was anticipated to be a human carcinogen [15], was the most toxic in the presence of visible light.

The acute toxicity of the phototoxic AQs to *D. magna* increased when UV-A and visible light were present in the spectrum relative to that in the presence of visible light only (Table 2). For 1-chloroanthraquinone and 1,8-dichloroanthraquinone, they showed a greater than 5-fold increase in the toxicity caused by the presence of UV-A (Table 2). This can be explained by the more strong absorption of UV-A radiation by them. In comparison, the acute toxicity of the AQs was weakly affected by the presence of UV-B (Table 2). The photoinduced toxicity of chemicals is associated with the types of light sources that affect the overlap between the emission spectra of the light sources used and the absorption spectra of the chemicals. Thus, it is necessary to assess the influence of the spectrum composition of different light sources on the photoinduced toxicity.

Table 1 showed that the log K_{OW} values (4.42 ~ 5.31) of the four most phototoxic AQs (compounds 1–4) were much higher than those (2.98 ~ 3.16) of the four least phototoxic AQs (compounds 11–14). The halogenated substituted (–Br or –Cl) AQs with large log K_{OW} values, tended to be much more phototoxic to *D. magna* than the hydroxyl and nitro substituted examples. Thus, the photoinduced toxicity of the AQs to *D. magna* is relevant to their hydrophobicity. Veith et al. [24] found that due to their low bioconcentration potential, some nitrotoluenes tested were not significantly phototoxic to *D. magna*.

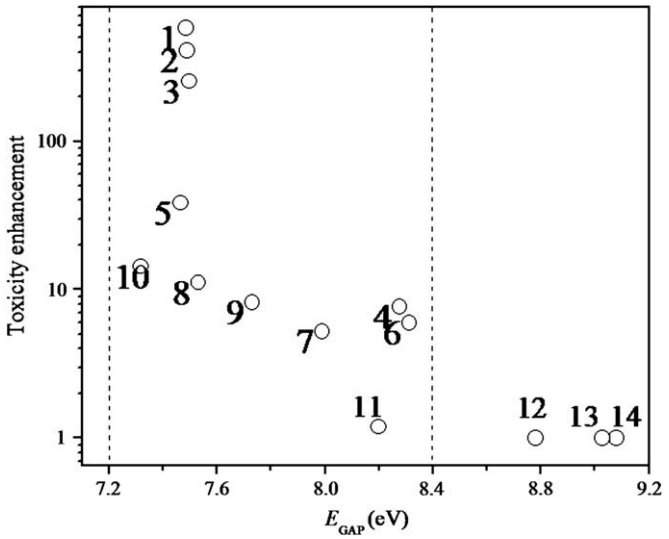

Fig. 2. Enhancement of toxicity caused by visible light. Dashed lines showed E_{GAP} ($E_{LUMO} - E_{HOMO}$) (7.8 ± 0.6 eV) where the studied anthraquinone derivatives exerted photoinduced toxicity to *Daphnia magna*. The acute toxicity increase was presented by $EC_{50(dark)}/EC_{50(visible\ light)}$. The sequence numbers of anthraquinone derivatives were given in Table 1.

4.2. Photoinduced toxicity assessment by energy gap

The E_{GAP} ($E_{LUMO} - E_{HOMO}$) of 14 AQs is listed in Table 1. Introduction of some auxochromes (-NH_2 > -OH > -Br > -Cl > -CH_3) of AQs resulted in the red-shift of their absorbance spectra (Table 1). It can be observed from Table 1 and Table 2 that the AQs with smaller E_{GAP} values exerted higher toxicity, which is mainly due to the better spectral overlap between the absorption spectra of AQs and the output spectrum of the light source. The plot of photoinduced toxicity (visible light/dark EC_{50} ratio) of 14 AQs with E_{GAP} is given in Fig. 2. The AQs exerted

Table 2
Acute toxicity of 14 anthraquinone derivatives to *Daphnia magna* under different light conditions.

Compound	EC_{50} (nmol/L)			
	Dark	Visible light	Visible light + UV-A	Simulated solar radiation
1-Amino-2,4-dibromoanthraquinone	>2500[a]	4.3[a]	2.9	1.2[a]
1-Amino-2-methyl-4-bromoanthraquinone	>5000	12.3	5.3	4.0
1-Amino-2-bromoanthraquinone	>5000	19.8	14.5	16.0
1,8-Dichloroanthraquinone	>5000	652.3	78.7	101.6
1,5-Diaminoanthraquinone	>5000	142.8	128.2	130.6
1-Chloroanthraquinone	>5000	837.0	156.6	225.2
1,8-Dihydroxyanthraquinone	>5000	959.3	702.7	254.4
1-Amino-4-bromoanthraquinone	>5000	449.2	398.3	286.7
1-Aminoanthraquinone	>5000	613.3	214.7	297.0
1-Amino-4-bromoanthraquinone-2-sulfonic acid	>10,000	698.4	572.5	483.3
1,2-Dihydroxyanthraquinone	>5000	4186.7	1494.7	>5000
1-Nitroanthraquinone	>10,000	>10,000	>10,000	>10,000
1,8-Dinitroanthraquinone	>4000	>4000	>4000	>4000
1,5-Dinitroanthraquinone	>10,000	>10,000	>10,000	>10,000

[a] Ref. [22].

photoinduced toxicity to *D. magna* when their E_{GAP} falls with the "window" of 7.2 eV ~ 8.4 eV. In comparison, E_{GAP} of the other three nitroanthraquinones (non-phototoxic) was greater than 8.7 eV. Thus, E_{GAP} was successfully used to indicate the photoinduced toxicity of AQs to *D. magna* in this study. E_{GAP} is a parameter that is used to characterize the molecular electronic structure related to light absorption [25–27]. Mekenyen et al. [25] found that PAHs exhibiting photoinduced toxicity to *D. magna* fell within an E_{GAP} "window" of 7.2 ± 0.4 eV. EGAP has also been proven to be a good indicator of the photoinduced toxicity in the other previous studies [9,24,28,29].

4.3. Photostability of phototoxic AQs

The control experiments showed the loss of all the tested AQs in culture medium was negligible in 48 h in the dark. Fig. 3 showed that nine out of eleven phototoxic AQs were photostable under visible light. Our previous study demonstrated that the photoproduct of 1-amino-2,4-dibromoanthraquinone was identified as a dimer [22]. The photoinduced toxicity of 1-amino-2,4-dibromoanthraquinone to *D. magna* decreased by a factor of 3.7 compared with the intact compound after 48 h photomodification [22]. Thus, photosensitization should be further investigated to explore the mechanism of the photoinduced toxicity of the AQs.

Table 3
First excitation triplet energies (E_{T1}, eV), vertical electron affinities (VEA, eV) and vertical ionization potentials (VIP, eV) at ground singlet state and excited triplet state of anthraquinone derivatives in water.

Compound	E_{T1}	VEA_{S0}	VEA_{T1}[a]	VIP_{S0}	VIP_1[b]
1-Amino-2,4-dibromoanthraquinone[c]	1.80	3.43	5.23	6.04	4.24
1-Amino-2-methyl-4-bromoanthraquinone	1.76	3.29	5.05	5.91	4.15
1-Amino-2-bromoanthraquinone	1.82	3.39	5.20	6.02	4.20
1,8-Dichloroanthraquinone	2.52	3.47	5.99	7.16	4.63
1,5-Diaminoanthraquinone	1.81	3.12	4.92	5.68	3.87
1-Chloroanthraquinone	2.51	3.45	5.96	7.18	4.67
1,8-Dihydroxyanthraquinone	2.25	3.41	5.66	6.48	4.23
1-Amino-4-bromoanthraquinone	1.74	3.31	5.05	5.90	4.16
1-Aminoanthraquinone	1.74	3.26	5.00	5.86	4.12
1,2-Dihydroxyanthraquinone	2.15	3.22	5.37	6.28	4.13

[a] $VEA_{T1} = VEA_{S0} + E_{T1}$.
[b] $VIP_{T1} = VIP_{S0} - E_{T1}$.
[c] Ref. [22].

4.4. Theoretical prediction of ROS production pathways of AQs

Photosensitization of AQs may occur through an electron transfer (type I) or energy transfer (type II) mechanism [30,31]. One of the most important ROS, singlet oxygen ($^1O_2$) can be produced through the direct energy transfer between the lowest triplet (T_1) state AQs and the ground state oxygen ($^3O_2$) (Eq. (1)). It can be seen

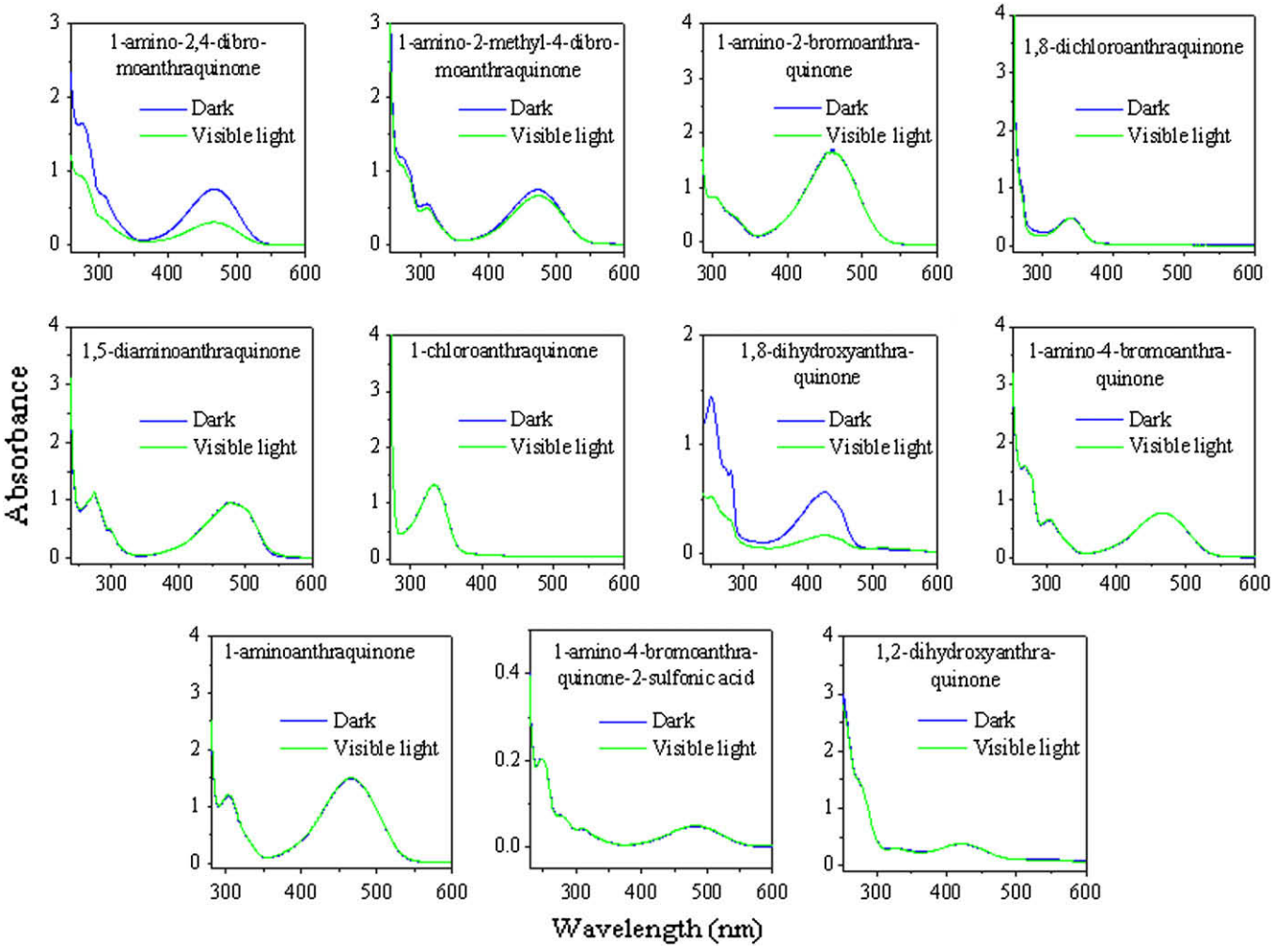

Fig. 3. Comparison of UV–visible absorption spectra of eleven anthraquinone derivatives in the dark or under visible light for 48 h.

from Table 3 that the first excitation triplet energies (E_{T1}) of the AQs are higher than the excited state energy of $^1O_2$ (1.05 eV) [32], suggesting that the AQs can generate $^1O_2$ through energy transfer upon the absorption of light.

$$AQs(T_1) + {}^3O_2 \rightarrow AQs(S_0) + {}^1O_2 \quad (1)$$

In addition, superoxide anion ($O_2^{\bullet -}$) may be generated through the direct electron transfer from the T1 state AQs. Whether the reaction can occur is governed by the vertical ionization potential (VIP) for T_1 state AQs and adiabatic electron affinity (AEA) for $^3O_2$ (3.87 eV). The VIP_{T1} is a measure of the reduction capacity from the T_1 state; the smaller the VIP_{T1}, the easier it is for the compound to be oxidized. For the AQs, their VIP_{T1} (Table 3) lies between 3.87 eV and 4.12 eV. Thus, it can be proposed that $^3O_2$ is unable to be reduced by the T_1 state AQs to generate $O_2^{\bullet -}$ (Eq. (2)).

$$AQs(T_1) + {}^3O_2 \rightarrow AQs^{\bullet +} + O_2^{\bullet -} \quad (2)$$

Another possible and important process is the autoionization with the formation of anion and cation radical couples, the T_1 state AQs may react with the surrounding ground singlet (S_0) state (Eq. (3)) or T_1 state AQs (Eq. (4)). In water, the vertical electron affinity (VEA) for T_1 state AQs is lower than their VIP_{S0} (Table 3). This indicates that Eq. (3) may not occur. However, $AQs^{\bullet -}$ may be generated through Eq. (4) according to their lower VIP_{T1} compared with their VEA_{T1} (Table 3). Moreover, AEA for $^3O_2$ (3.87 eV) is much higher than VEA_{S0} of AQs (3.12 eV ~ 3.47 eV). Thus, $AQs^{\bullet -}$ may transfer an electron to $^3O_2$ with the generation of $O_2^{\bullet -}$ through Eq. (5).

$$AQs(T_1) + AQs(S_0) \rightarrow AQs^{\bullet -} + AQs^{\bullet +} \quad (3)$$

$$AQs(T_1) + AQs(T_1) \rightarrow AQs^{\bullet -} + AQs^{\bullet +} \quad (4)$$

$$AQs^{\bullet -} + {}^3O_2 \rightarrow AQs + O_2^{\bullet -} \quad (5)$$

It can be concluded that the AQs are able to generate $^1O_2$ through direct energy transfer and $O_2^{\bullet -}$ through autoionization followed by the electron transfer of anion radicals. Some previous studies also successfully explored the phototoxic reactions of chemicals by TD-DFT [32–35].

5. Conclusions

The present study indicated that some AQs resulted in highly acute photoinduced toxicity to *D. magna* and the presence of UV light generally enhanced the acute toxicity of the AQs. The E_{GAP} may be used to distinguish the phototoxic AQs to *D. magna* from non-phototoxic ones. The pathway of phototoxic reactions of the AQs was proposed by TD-DFT calculations. ROS including superoxide anion and singlet oxygen may be generated through type I and type II photosensitization reactions. It is likely that E_{GAP} and TD-DFT can be applied to the phototoxic study of other photosensitive chemicals such as naphthoquinones and quinolones. This study provided part of the theoretical evidence in support of ecological risk assessment for AQ dyes and development of environmental-friendly dyes.

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