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# Theoretical study on the photophysical and photochemical characteristics of aluminum ion-complexed perylenequinone

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## Abstract

The photophysical and photochemical characteristics of the aluminum ion-complexed perylenequinone ($Al^{3+}$-PQ) at different chain length have been explored employing the quantum chemical method in this paper. It is revealed firstly, the optimized structures of the complexes at different chain lengths are all one-dimension polymeric chains in the ground state. Secondly, the chelation reaction not only decreases the molecular $E_{HOMO}$, $E_{LUMO}$ and $\Delta E$, but also shifts the excitation spectra bathochromatically. In addition, based on the present calculation results, the first triplet excitation energy of the complexes at different chain length can directly be transferred to molecular oxygen to generate the singlet excited molecular oxygen ($^1O_2$) (Type II). On the contrary, the semiquinone anion radicals ($Al^{3+}$-$PQ^{\bullet -}$) cannot react with triplet molecular oxygen to form the superoxide anion radical ($O_2^{\bullet -}$), which indicates photosensitization mechanism Type I is not involved in the photodynamic action of $Al^{3+}$-PQ.
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*Keywords:* Perylenequinonoid derivatives; Perylenequinone; Aluminium ion; Active oxygen; Photosensitization mechanism

## 1. Introduction

Photodynamic therapy (PDT) is a recently developed cancer treatment method that employs both selective photosensitizer and powerful light source, which matches the absorption spectrum of photosensitizer [1,2]. With the development of laser technique, photosensitizer becomes the key factor in this field. Much work has been devoted to develop new generation ones and explore their photosensitization mechanisms as well. Perylenequinonoid derivatives (PQD), such as hypocrellin A (HA) and hypocrellin B (HB) (Fig. 1), have attracted considerable attention owing to their excellent properties of photosensitization [3–11]. For two decades, PQD have been investigated widely at aspect of photophysics, photochemistry, photobiology, which revealed PQD's great potential of being developed as new generation photosensitizer.

Nevertheless, PQD have poor water solubility and show weak absorption in the therapeutic window, in which tissue penetration is maximal [12,13]. These disadvantages limit their PDT applications clinically.

Previous studies demonstrated that the chelation of HA with metals, such as $B^{3+}$, $Mg^{2+}$, $Zn^{2+}$, $Cu^{2+}$ can improve notably their water solubility and make the absorption of PQD bathochromic shift [14,15]. Hu and co-workers [16] investigated the chelation of HA with aluminum ion ($Al^{3+}$) and the photodynamic action of the resulting complex. They found that the complex $Al^{3+}$-HA had much higher solubility and stability in water than that of other metal complexes of HA. In addition, $Al^{3+}$-HA not only preserved the $^1O_2$-generating function of its parent compound but also enhanced significantly the production yields of $O_2^{\bullet -}$ in the presence of electron donors as well. To our knowledge, little work has been done on the photosensitization mechanisms of the metal–ion complex of PQD. Previous reports revealed that perylenequinone (PQ) is the active center of PQD and it is important to reserve their photosensitive activity [9,17,18].

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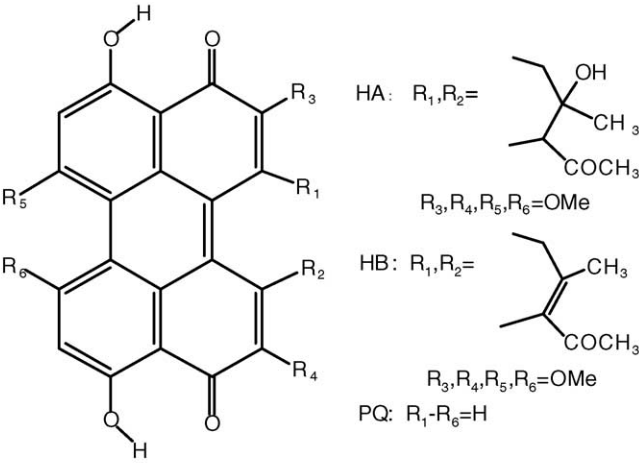

Fig. 1. Chemical structures of PQD.

In this paper, we designed some model compounds of $Al^{3+}$-PQ at different chain length and investigated in detail their photophysical and photochemical properties employing the quantum chemical method.

## 2. Methods

Based on the pattern of chelation of PQ with $Al^{3+}$, PQ-$Al^{3+}$-PQ was designated as a fundamental structure ($n=1$). The $Al^{3+}$-PQ unit was added at one end with the increasing of chain length and the complexes of $n$ from 1 to 7 have been calculated.

The structures of the ground state were firstly fully optimized employing the semi-empirical AM1, PM3 and MNDO methods. With the calculated structures for AM1 as starting points, the excited state structures were optimized with ZINDO/S method, which has been proved efficiently in the calculation of excitation energy of this kind of organic molecules [19]. All work has been done with GAUSSIAN 98 package of programs [20].

## 3. Results and discussion

### 3.1. Structure of the complexes

Hu and co-workers [16] proposed a probable polymeric cationic structure for $Al^{3+}$-HA. Similar structure has also been proposed for the complex of DHAQ with some non-transition metal ions [21] and $Cu^{2+}$ [22]. We optimized the $Al^{3+}$-PQ for $n$ from 1 to 7 and found that the resulting structures of the complexes were all one-dimension polymeric chains in the ground state. The structure of the complex ($n=4$) has been shown in Fig. 2, from which it can also be seen that the adjacent units are almost vertical to each other in the polymeric chains.

### 3.2. The frontier molecular orbital energy

The frontier molecular orbital energy for PQ and the complexes at different chain length obtained by AM1, PM3 and MNDO methods are shown in Table 1. It can be seen that the results of the three semi-empirical methods are comparative.

As shown in Table 1, the chelation of PQ with $Al^{3+}$ makes molecular HOMO energy ($E_{\mathrm{HOMO}}$), LUMO energy ($E_{\mathrm{LUMO}}$) and $\Delta E$ ($E_{\mathrm{LUMO}}-E_{\mathrm{HOMO}}$) lower. The results indicate that the donor electron ability of molecule decreases, while the acceptor electron ability enhances. The sketch map of $E_{\mathrm{HOMO}}$, $E_{\mathrm{LUMO}}$ and $\Delta E$ obtained with AM1 against the chain length were illustrated in Figs. 3–5. It follows that the $E_{\mathrm{HOMO}}$, $E_{\mathrm{LUMO}}$ and $\Delta E$ of the complexes all correlate well with chain length. The longer of polymeric chain is, the lower of the frontier orbital energy and $\Delta E$ are. The energy gap between $E_{\mathrm{HOMO}}$ and $E_{\mathrm{HOMO}}$ becomes smaller and smaller as the chain length increases, suggesting the complexes' great potential as electric conductor material as well.

The frontier molecular orbital figurations for PQ and the complexes were also sketched by means of a three-dimension molecular modeling program CHEM3D (Fig. 6). These figures show that the transitions from HOMO to LUMO are all $\pi \rightarrow \pi^*$ type and the $Al^{3+}$ does not contribute to HOMO and LUMO. As the complex of $n=1$ is concerned, the two PQ

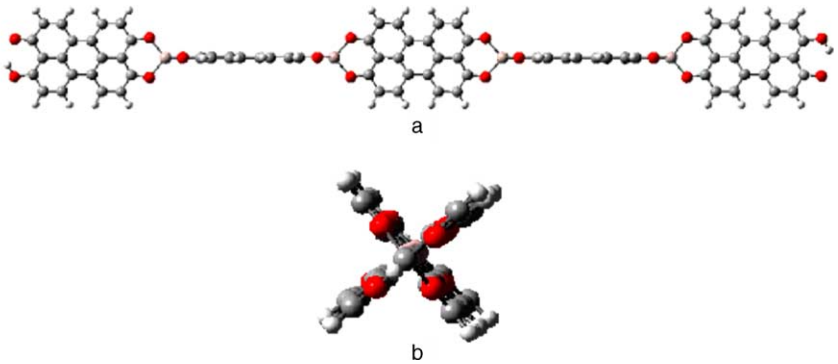

Fig. 2. Optimized structure for the complex of $n=4$.

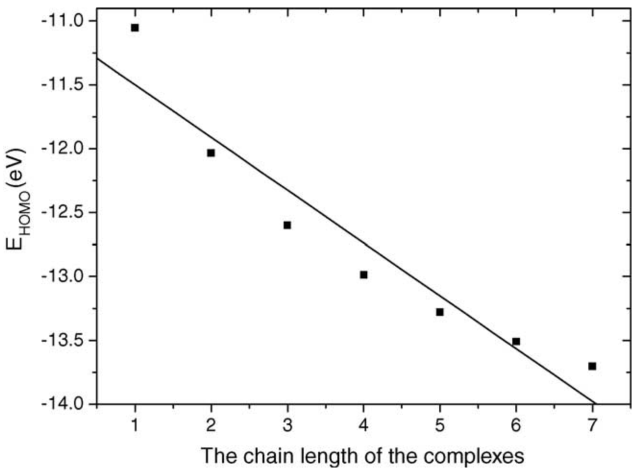

Fig. 3. The chain length against the HOMO energy level of the complexes.

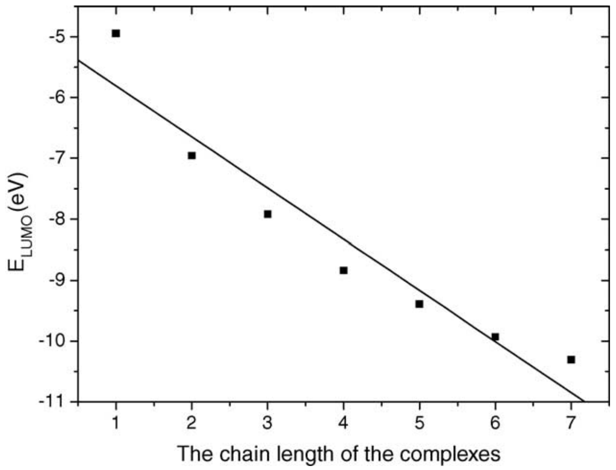

Fig. 4. The chain length against the LUMO energy level of the complexes.

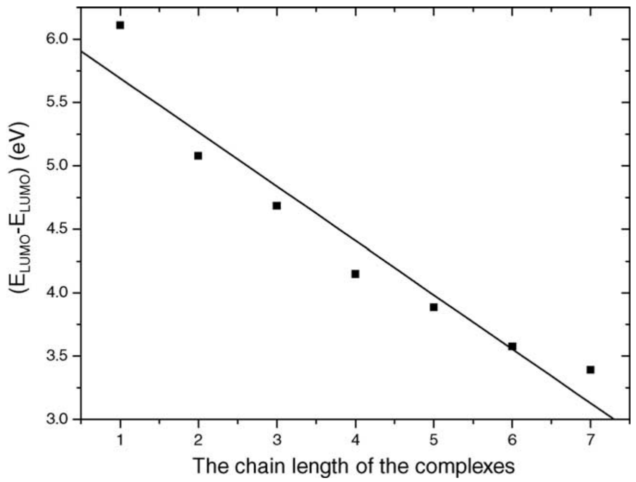

Fig. 5. The chain length against the energy gap of HOMO and LUMO of the complexes.

Table 1
The frontier molecular orbital energy properties (eV)

| Compounds | AM1 | PM3 | MNDO |
|---|---|---|---|
| PQ | | | |
| HOMO | −8.901 | −8.870 | −8.718 |
| LUMO | −2.209 | −2.272 | −1.887 |
| $\Delta E$ | 6.692 | 6.598 | 6.831 |
| 1 | | | |
| HOMO | −11.054 | −11.035 | −10.845 |
| LUMO | −4.944 | −4.984 | −4.713 |
| $\Delta E$ | 6.110 | 6.050 | 6.132 |
| 2 | | | |
| HOMO | −12.034 | −12.025 | −11.813 |
| LUMO | −6.957 | −6.973 | −6.776 |
| $\Delta E$ | 5.077 | 5.052 | 5.037 |
| 3 | | | |
| HOMO | −12.601 | −12.604 | −12.372 |
| LUMO | −7.918 | −7.954 | −7.735 |
| $\Delta E$ | 4.683 | 4.650 | 4.637 |
| 4 | | | |
| HOMO | −12.987 | −13.001 | −12.754 |
| LUMO | −8.841 | −8.892 | −8.658 |
| $\Delta E$ | 4.146 | 4.109 | 4.096 |
| 5 | | | |
| HOMO | −13.278 | −13.301 | −13.042 |
| LUMO | −9.392 | −9.459 | −9.205 |
| $\Delta E$ | 3.886 | 3.841 | 3.837 |
| 6 | | | |
| HOMO | −13.510 | −13.540 | −13.273 |
| LUMO | −9.935 | −10.017 | −9.745 |
| $\Delta E$ | 3.575 | 3.523 | 3.528 |
| 7 | | | |
| HOMO | −13.703 | −13.743 | −13.465 |
| LUMO | −10.311 | −10.300 | −10.119 |
| $\Delta E$ | 3.393 | 3.443 | 3.346 |

units are in equivalent position and thus, the frontier orbital shows same nodal surface and shape.

### 3.3. Excited states and photophysical process

In photochemical process, the photosensitizer are initiated firstly by excitation from ground state to first singlet excited state and then the electron transfer from singlet to triplet by intersystem crossing. It is well known that the photosensitization reaction usually occurs in the lowest triplet state. The excitation energies and oscillator strengths for the five lowest singlet excitations of PQ and the complexes at different chain length are listed in Table 2. It can be seen that the chelation reaction shifts the excitation spectra bathochromatically. The maximum wavelength is 449 nm for complex of $n = 2$. The excitation spectra for complexes of $n > 5$ are very similar and the absorption peaks are all about 430 nm.

The lowest triplet excitation energy of PQ and complexes have also been obtained and given in Table 3. It can be concluded from the data that the chelation reaction decreases the $T_1$ energy. The $T_1$ energy of the complexes all lie more than

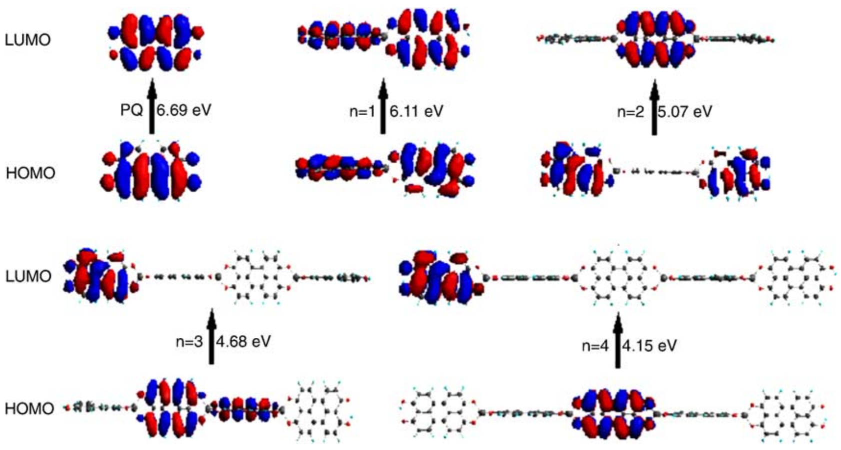

Fig. 6. HOMO and LUMO for PQ and the complexes.

1.6 eV and increases with the chain length, but when $n > 5$ the $T_1$ energy change little.

The sketch map of the chain length against $S_1 \rightarrow T_1$ energy gap of the complexes are illustrated in Fig. 7. The general trend is that the energy gap decreases as the chain length increases and approaches a constant ultimately. It can be seen that the complex of $n = 2$ has the lowest $S_1 \rightarrow T_1$ energy gap (1.07 eV) and thus possesses the highest triplet-generating quantum yields theoretically.

Table 2
The singlet excitation energies and oscillator strengths of the complexes

| | | | | | |
|---|---|---|---|---|---|
| PQ | | | | | |
| $^1$E (eV) | 2.91 | 2.92 | 2.94 | 3.27 | 4.02 |
| λ (nm) | 426 | 424 | 422 | 379 | 309 |
| *f* | 0.00 | 0.00 | 0.23 | 1.02 | 0.09 |
| 1 | | | | | |
| $^1$E (eV) | 2.81 | 2.82 | 3.19 | 3.29 | 3.40 |
| λ (nm) | 441 | 439 | 389 | 377 | 365 |
| *f* | 0.86 | 0.42 | 1.76 | 0.01 | 0.01 |
| 2 | | | | | |
| $^1$E (eV) | 2.76 | 2.81 | 2.82 | 3.15 | 3.26 |
| λ (nm) | 449 | 441 | 439 | 393 | 381 |
| *f* | 0.53 | 0.50 | 0.91 | 2.97 | 0.03 |
| 3 | | | | | |
| $^1$E (eV) | 2.79 | 2.79 | 2.88 | 2.88 | 3.16 |
| λ (nm) | 445 | 445 | 431 | 430 | 393 |
| *f* | 0.44 | 0.45 | 1.37 | 0.68 | 3.92 |
| 4 | | | | | |
| $^1$E (eV) | 2.88 | 2.88 | 2.89 | 2.90 | 2.90 |
| λ (nm) | 431 | 430 | 430 | 428 | 428 |
| *f* | 0.00 | 1.36 | 0.26 | 0.02 | 2.40 |
| 5 | | | | | |
| $^1$E (eV) | 2.87 | 2.87 | 2.89 | 2.89 | 2.90 |
| λ (nm) | 432 | 432 | 430 | 430 | 427 |
| *f* | 0.38 | 0.37 | 0.73 | 0.69 | 1.59 |
| 6 | | | | | |
| $^1$E (eV) | 2.87 | 2.87 | 2.88 | 2.89 | 2.90 |
| λ (nm) | 432 | 432 | 431 | 430 | 428 |
| *f* | 0.09 | 1.27 | 0.02 | 0.76 | 0.77 |
| 7 | | | | | |
| $^1$E (eV) | 2.87 | 2.87 | 2.88 | 2.88 | 2.90 |
| λ (nm) | 432 | 432 | 430 | 430 | 428 |
| *f* | 0.64 | 0.64 | 0.52 | 0.50 | 1.51 |

Table 3
The three lowest triplet energies in eV (nm)[a,b]

| Compounds | T1 | T2 | T3 |
|---|---|---|---|
| 1 | 1.653 (750.05) | 1.653 (750.03) | 2.186 (567.11) |
| 2 | 1.690 (733.84) | 1.690 (733.80) | 1.724 (719.24) |
| 3 | 1.688 (734.51) | 1.688 (734.51) | 1.896 (654.08) |
| 4 | 1.793 (691.67) | 1.793 (691.67) | 1.892 (655.26) |
| 5 | 1.800 (688.74) | 1.800 (688.74) | 1.887 (657.20) |
| 6 | 1.798 (689.49) | 1.798 (689.47) | 1.893 (654.92) |
| 7 | 1.798 (689.94) | 1.797 (689.93) | 1.892 (655.38) |

[a] These transitions are forbidden; all extinction coefficient are therefore zero.

[b] The TD-DFT calculated results of the complex for $n = 1$.

### 3.4. Photosensitization mechanism of the complexes

It has been demonstrated that there are mainly two possible photosensitization mechanism for PQD [23–25].

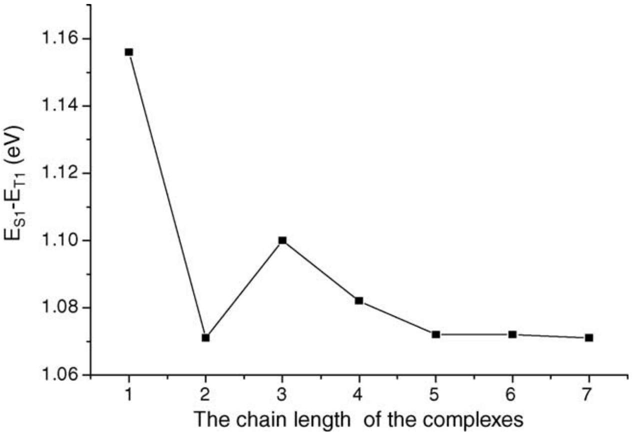

Fig. 7. The chain length against $S_1 \rightarrow T_1$ energy gap of the complexes.

Table 4
Vertical electron affinities (VEA) in eV of the complexes

| Compounds | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| VEA | 6.312 | 7.978 | 9.116 | 9.949 | 10.605 | 11.454 |

Type I:

$$\mathrm{PQD(T_1)} + \mathrm{D} \rightarrow \mathrm{PQD}^{\bullet-} + \mathrm{D}^{\bullet+}$$

$$\mathrm{PQD}^{\bullet-} + {}^{3}\mathrm{O_2} \rightarrow \mathrm{PQD} + \mathrm{O_2}^{\bullet-}$$

Type II:

$$\mathrm{PQD(T_1)} + {}^{3}\mathrm{O_2}({}^{3}\textstyle\sum) \rightarrow \mathrm{PQD(S_0)} + {}^{1}\mathrm{O_2}({}^{1}\Delta_{\mathrm{g}})$$

Singlet excited molecular oxygen (${}^{1}O_2$) generated through the mechanism Type II is now generally considered to be an active PDT intermediate [26]. In this case, the deexcitation energy of $T_1$ state for $Al^{3+}$-PQ should thus be larger than the energy needed to excite molecular oxygen to reactive ${}^{1}\Delta_g$ state. The latter is approximately 1.234 eV according to our calculated result. The energy of $T_1$ state for all complexes is greater than 1.234 eV as shown in Table 1. Thus, the energy transfer from complexes to molecular oxygen to generate ${}^{1}O_2$ should in principle be possible.

In oxygen Type I reaction, the triplet state of the photosensitizer may react with an electron donor to form the $PQD^{\bullet-}$. The reaction is followed by electron transfer from the $PQD^{\bullet-}$ to molecular oxygen resulting in formation of reactive superoxide anion radicals and regeneration of the ground state photosensitizer [27–29]. The adiabatic electron affinity (AEA) of molecular oxygen ${}^{3}O_2$ is 0.213 eV (expt. 0.451 eV [30]) at present calculation level, which should be larger than the ground state vertical electron affinity (VEA) of the complexes if Type I can occur. Nevertheless, the delocalization of positive charge for $Al^{3+}$ over the conjugative system during the $Al^{3+}$-PQ formation makes the VEA of the complexes increase significantly. It can be seen from Table 4 that VEA of the complexes is much larger than AEA of ${}^{3}O_2$. The result suggests that the extra electron cannot be directly transferred to molecular oxygen for the large energy gap, which indicates the mechanism Type I is not involved in the photosensitization process of $Al^{3+}$-PQ. According to Hu and co-worker's [16] result, the $Al^{3+}$-HA possess higher $O_2^{\bullet-}$ generation yields than its parent. Based on our theoretical result, $O_2^{\bullet-}$ is most likely generated from the mechanism Type II in which ${}^{1}O_2$ can react further with an electron donor [31].

## 4. Conclusion

The photophysical and photochemical behavior of a new photosensitizer –$[Al^{3+}\text{-PQ}]_n$ ($n$ = 1–7) were studied by semi-empirical methods. The results indicate that the optimized structures of the complexes at different chain lengths are all one-dimension polymeric chains. With the increasing of the chain length the $\Delta E$ gets smaller, which suggests the complexes' great potential as electric photochemical material as well. Moreover, $O_2^{\bullet-}$ is most likely generated from the mechanism Type II in which ${}^{1}O_2$ can react further with an electron donor, rather than Type I.

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