Dyes and Pigments 85 (2010) 21–26

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Photoinduced energy and electron transfer in porphyrin-anthraquinone dyads bridged with a triazine group

Minli Tao [a,b], Lizeng Liu [a,c], Dongzhi Liu [a], Xueqin Zhou [a,*]

[a] School of Chemical Engineering, Tianjin University, Tianjin 300072, PR China
[b] Tianjin University R&D Center for Petrochemical Technology, Tianjin 300070, PR China
[c] College of Science, Tianjin University of Commerce, Tianjin 300134, PR China

ARTICLE INFO

Article history:
Received 20 March 2009
Received in revised form
17 September 2009
Accepted 24 September 2009
Available online 1 October 2009

Keywords:
Energy transfer
Electron transfer
Charge-separated state
Porphyrin
Dyad
Synthesis

ABSTRACT

Porphyrin-anthraquinone dyads containing a triazine group as linker were synthesized and characterized by ^{1}H NMR, UV–visible, fluorescence and transient spectra and ESI-MS. Absorption spectra revealed that there was no appreciable interaction between the ground-state porphyrin moiety and the ground-state anthraquinone moiety. Fluorescence spectra illustrated that energy transfer takes place from the excited anthraquinone moiety to the porphyrin moiety when excited at 250 nm, whilst efficient electron transfer occurs from the singlet excited porphyrin moiety to the anthraquinone moiety in the case of excitation at 420 nm. A long-lived, charge-separated state $H_2P^{\bullet+}–EQ^{\bullet-}$ was observed by transient absorption spectra with a lifetime of 1.42 μs and 1.33 μs. These photochemical events were explained from electrochemical studies and suggest that the compounds have the ability to simulate electron transfer from chlorophylls to electron acceptors.

1. Introduction

Photosynthetic reaction centers, which convert solar energy into useful chemical energy, consist of a protein matrix and donor-acceptor redox active pigments. During photosynthesis, the primary electron transfer (ET) step occurs from a porphyrin-based complex [1,2] and, subsequently, the excited porphyrin–base complex donates an electron to (bacterio) chlorophylls or their corresponding dimers and thence to bacteriopheophyrins and quinone acceptors Q_A and Q_B [3], resulting in a long-lived, charge-separated state. To gain better insight into the photosynthetic process, numerous model molecules have been reported [3–8] and the dependencies of both the intramolecular/intermolecular ET rate and the charge-separated-state lifetime on donor-acceptor distance, relative orientation and coupling energies have been investigated using different optical and magnetic resonance techniques [3,9–11].

Porphyrin dyads/triads have received much attention owing to their variety and their important role in biology, particularly photosynthesis [1]. Quinone [12–15], anthraquinone [16], and recently fullerenes [1,17,18] are common electron acceptors in these molecules because of their wide absorption range, low LUMO-(lowest unoccupied molecular orbital), and small reorganizational energies which can accelerate the forward ET process and retard the back ET process [19]. However, electronic coupling of the donor and acceptor depends not only on the donor-acceptor distance, but also on the electronic properties of the linkers as described by Marcus [20]. Thus, different bridging groups have been explored as linkages between donors and acceptors and the influence of the electronic properties of the linkers on the ET process have been investigated.

The present authors have investigated the synthesis and optical properties of porphyrin-oxadiazole dyads bridged by either an azo group or a triazine group and found that the triazine linker favours intramolecular photoinduced ET from the excited oxadiazole moiety to the porphyrin moiety but effectively blocks ET from the excited porphyrin moiety to the oxadiazole moiety [21]. This paper concerns the synthesis of porphyrin-anthraquinone dyads linked by a triazine group (Fig. 1) and the study of their spectral properties, intramolecular energy and electron transfer.

2. Experimental

2.1. General

5-(4-Aminophenyl)-10,15,20-triphenylporphyrin (**ATPP**) and aminoethyl amino-anthraquinone (**AEAQ**) were prepared as

---

[*] Corresponding author. Tel./fax: +86 22 27400911.
E-mail address: zhouxueqin@tju.edu.cn (X. Zhou).

0143-7208/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2009.09.012

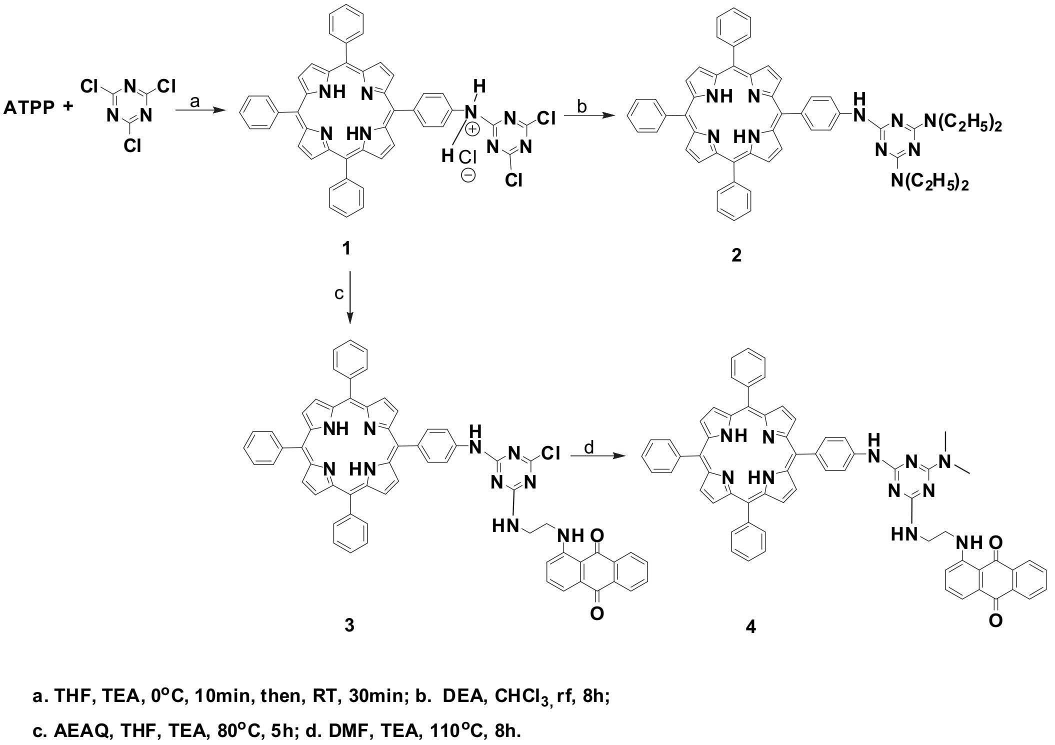


Fig. 1. Synthesis of porphyrin-anthraquinone dyads connected with a triazine group.

reported [22,23]. All other reagents and solvents were reagent grade and further purified by the standard methods if necessary. Infrared spectra were recorded on a Bio-rad FTS3000. ^{1}H NMR spectra were obtained on a Varian UNITY-PLUS400 spectrometer. FAB and ESI mass spectra were obtained on a VG ZAB-HS mass spectrometer and Finnigan LCQ mass spectrometer respectively. Absorption spectra were taken on a Thermo Spectronic, Helios Gamma spectrometer. Fluorescence spectra were recorded on a Varian CARY ECLIPSE fluorospectrophotometer. Electrochemical properties were measured using a BAS 100W electrochemical analyzer and performed in a three-electrode cell. A glassy carbon electrode was used as working electrode, Ag/AgNO$_3$ electrode as reference electrode and platinum as auxiliary electrode. Scan rates were 100 mV/s. Dichloromethane with 0.05 mol/L tetrabutylammonium hexafluorophosphate (TBAPF$_6$) was employed as the medium for all the cyclic voltammetric experiments. Nanosecond transient absorption spectra were recorded by LP920 laser-flash photolysis apparatus with 532 nm light, Nd: YAG laser used as the exciting source and a pulsed xenon flash lamp as monitor light. All the solutions were purged using nitrogen gas prior to the transient absorption spectral and electrochemical measurement.

2.2. Synthesis

2.2.1. 5-(4-(3,5-Dichloro triazine) aminophenyl)-10,15,20–triphenyl porphyrin hydrochloride (**1**)

A solution of 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (**ATPP**) 25 mg (0.04 mmol) in THF (1.0 mL) was added to a THF (2.0 mL) solution of cyanuric chloride (7.3 mg, 0.04 mmol) and triethanolamine (TEA) (4.8 mg, 0.048 mmol) at 0 °C. After stirring at 0 °C for 10 min, the solution was left to warm to room temperature and react for 30 min with thin layer chromatography (TLC) monitoring to indicate the completion of the reaction. After the reaction completed, the mixture was evaporated in vacuum. Compound **1** was purified by column chromatography on silica gel eluted with petroleum ether/ethyl acetate (2:1 v/v). The title product was

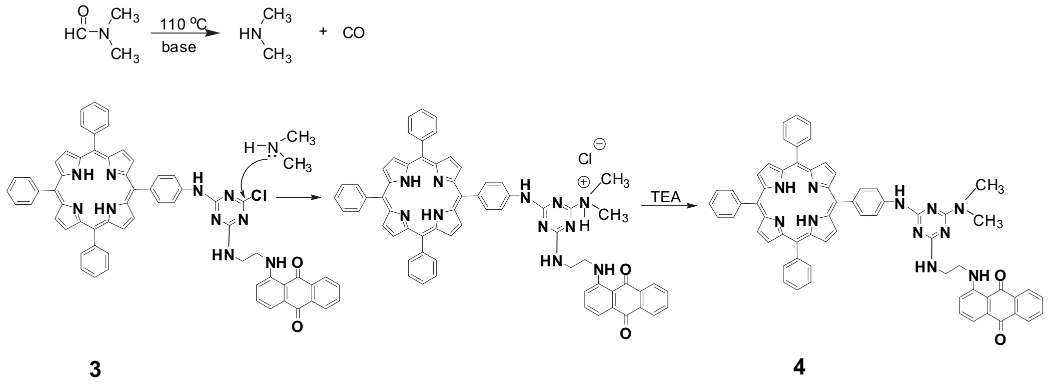


Fig. 2. Reaction mechanism for the conversion of **3** to **4**.

isolated as blue violet solid 29 mg (90.6%) yield, mp>300 °C; ^{1}H NMR ($CDCl_3$, ppm), δ: 8.92–8.91 (d, $J = 4.8$ Hz, 2H, C_4H_5N β-H), 8.88–8.86 (d, $J = 6.0$ Hz, 6H, C_4H_5N β-H), 8.24–8.19 (m, 8H, $-C_6H_5$), 8.01–7.99 (d, $J = 8.0$ Hz, 2H, $-C_6H_5$), 7.79–7.74 (m, 10H, $-C_6H_5$, $-NH\cdot\underline{H}Cl$), 7.45 (s, 1H, –NH), −2.72 (s, 2H, NH); ESI-MS (*m/z*): 814.4 (M^++HCl).

2.2.2. 5-[4-(3,5-Bi-diethylamino triazine) aminophenyl]-10,15,20–triphenyl porphyrin (*2*)

Compound **1** (32 mg, 0.04 mmol) was dissolved in $CHCl_3$ (15 mL), while stirring, diethylamine (DEA, 7.3 mg, 0.1 mmol) were added. The mixture was stirred at refluxing temperature for 8 h. The reaction mixture was washed with water and dried overnight with $MgSO_4$. The compound was purified by column chromatography on silica gel using $CHCl_3$/acetone (30:1 v/v) as eluent. The title product was isolated as blue violet solid 31 mg (88.6%) yield, mp>300 °C. ^{1}H NMR ($CDCl_3$, ppm), δ: 8.90 (s, 8H, C_4H_5N β-H), 8.23–8.21 (d, $J = 4.0$ Hz, 8H, $-C_6H_5$), 7.80–7.77 (m, 11H, $-C_6H_5$), 5.30 (s, 1H, $-C_6H_5\underline{NH}$), 3.68 (s, 12H, $-\underline{CH_2}CH_3$), 1.80 (s, 8H, $-CH_2\underline{CH_3}$), −2.76 (s, 2H, NH); FAB-MS (*m/z*): 851.0 (M^+).

2.2.3. 5-{4-[3-Chloro-5-(aminoethyl amino-anthraquinone) triazine] aminophenyl}-10,15,20–triphenyl porphyrin (*3*)

AEAQ (26.7 mg, 0.1 mmol) and TEA (4.8 mg, 0.048 mmol) were added to the THF (5.0 mL) solution of compound **1**. The mixture was stirred at 80 °C for 5 h with TLC monitoring the completion of the reaction. The solvent was removed and the residue was purified by column chromatography on silica gel using CH_2Cl_2/ethyl acetate (100:1 v/v) as eluent. The title product was isolated as blue violet solid 27 mg (72%) yield, mp > 300 °C. ^{1}H NMR ($CDCl_3$, ppm), δ: 9.90 (s, 1H, $C_{14}H_7O_2\underline{NH}$), 8.95 (s, 8H, C_4H_5N β-H), 8.57 (s, 1H, ArH), 8.21 − 8.14 (m, 10H, ArH), 7.88 − 7.84 (m, 4H, ArH), 7.77 − 7.68 (m, 12H, $-C_6H_5$), 3.82 (s, 1H, $-C_6H_5NH$), 3.68 − 3.72 (m, 4H, $-CH_2$), −2.77 (s, 2H, NH); ESI-MS (*m/z*): 1007.5 (M^+); Anal. Calcd. for $C_{63}H_{43}ClN_{10}O_2$: C, 75.10; H, 4.30; N, 13.90. Found: C, 74.52; H, 4.34; N, 13.79.

2.2.4. 5-{4-[3-Dimethylamino-5-(aminoethyl amino-anthraquinone) triazine] aminophenyl}-10,15,20–triphenyl porphyrin (*4*)

Compound **3** (40 mg, 0.04 mmol) was dissolved in DMF (4 mL), while stirring, **AEAQ** (26.7 mg, 0.1 mmol) and TEA (4.8 mg, 0.048 mmol) were added. The mixture was heated to 110 °C for 8 h. The solvent was removed and the residue was purified by column chromatography on silica gel using CH_2Cl_2/CH_3OH (30:1 v/v) as eluent. The title product was isolated as blue violet solid 17 mg (42%) yield, mp>300 °C. ^{1}H NMR ($CDCl_3$, ppm), δ: 9.92 (s, 1H, $C_{14}H_7O_2\underline{NH}$), 8.89–8.88 (m, 8H, C_4H_5N β-H), 8.40 (s, 1H, ArH), 8.22–8.10 (m, 12H, ArH), 8.00 (s, 2H, ArH), 7.76–7.70 (m, 12H, $-C_6H_5$), 3.88 (s, 1H, $-C_6H_5\underline{NH}$), 3.64–3.60 (m, 2H, ArH–$\underline{CH_2}$), 3.30 (s, 2H, ArH–$\underline{CH_2}$), 3.21–3.17 (m, 6H, $-N(CH_3)_2$), −2.78 (s, 2H, NH); FAB-MS (*m/z*): 1016.4 (M^+); Anal. Calcd. for $C_{65}H_{49}N_{11}O_2$: C, 76.83; H, 4.86; N, 15.16. Found: C, 76.21; H, 4.92; N, 15.29.

3. Results and discussion

3.1. Synthesis

Compound **1** was synthesized in high yield from aminoporphyrin **ATPP** and cyanuric chloride with TEA as the acid binding agent. The obtained compound **1** exists as the hydrochloride form (Fig. 1), which could be confirmed by the ESI-MS determination. The ^{1}H NMR spectrum of compound **1** shows an additional H atom at $\ddot{a} = 7.79 - 7.74$, which is assigned to the hydrochloride H atom. Compound **2** and **3** were prepared from compound **1** by introduction of additional group in the triazine circle. Compound **4** was synthesized conveniently through heating compound **3** in DMF. The mechanism was suggested in Fig. 2 and might be relative to the decomposition of DMF under heating [24–26]. And this decomposition reaction is catalysed by acidic and basic materials [24].

3.2. Absorption property of porphyrin-anthraquinone dyads

The steady-state absorption spectra of dyad **4** along with reference compounds **AEAQ** and **ATPP** in dichloromethane are shown in Fig. 3. The absorption spectrum of dyad **4** is identical with the sum of the spectra of porphyrin **ATPP** and compound **AEAQ**, indicating that there is no appreciable interaction between porphyrin moiety and anthraquinone moiety in the dyad **4** in the ground-state [1]. The band in the **UV** region is primarily due to the absorption of the anthraquinone moiety. The band at about 420 nm is the Soret band of the porphyrin moiety, which is an $a_{1u}(\pi) \rightarrow e_g(\pi^*)$ electron transition, assigned to the second excited state S_2 generated by $\pi \rightarrow \pi^*$ transition. The weak absorption bands between 500 nm and 660 nm are the Q band of the porphyrin moiety and corresponds to an $a_{2u}(\pi) \rightarrow e_g(\pi^*)$ electron transition, belonging to the first excited state S_1 generated by $\pi \rightarrow \pi^*$ transition [27,28]. Furthermore, the absorption of **AEAQ** at 250 nm had no overlap with the absorption of **ATPP**. Hence, the **AEAQ** moiety of the dyad is expected to be selectively excited by irradiation at 250 nm; while the porphyrin moiety could be excited under exposure to light of 420 nm, 517 nm, 554 nm, 592 nm, or 648 nm.

3.3. Energy transfer and electron transfer of porphyrin-anthraquinone dyads

3.3.1. Excitation on the anthraquinone moiety

Fig. 4 shows the fluorescence emission spectra of dyad **4**, along with that of porphyrin **ATPP** and compound **AEAQ** excited at 250 nm. The bands at about 500 nm and 600 nm are the double waves of excited and emission bands. The dyad **4** revealed three emission bands: one is at 306 nm which corresponds to the emission of anthraquinone moiety, and the others are at 650 nm and 717 nm in accord with the emission of the porphyrin moiety. The emission intensity of the 306 nm band in the dyad **4** was found to be quenched almost completely as compared to the reference compound **AEAQ**. However the intensity at 650 nm, 720 nm bands

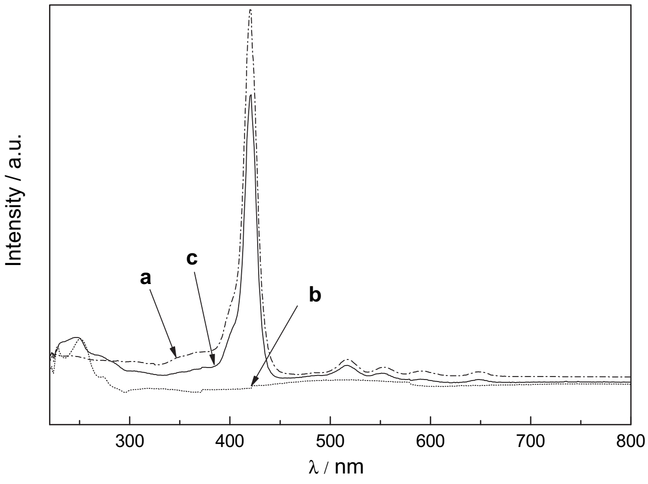


Fig. 3. Steady-state absorption spectra of (a) 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (**ATPP**), (b) aminoethyl amino-anthraquinone (**AEAQ**), and (c) porphyrin-anthraquinone dyad **4** in dichloromethane. The concentrations were held at 5×10^{-6} mol/L.

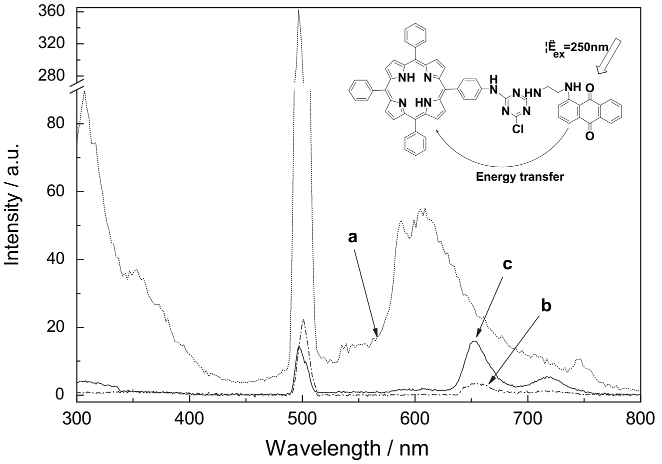


Fig. 4. Fluorescence emission spectra of (a) **AEAQ**, (b) **ATPP** and (c) porphyrin-anthraquinone dyad **4** in dichloromethane. The concentrations were held constant to 5×10^{-6} mol/L for all of the species. $\lambda_{ex} = 250$ nm.

increased compared to compound **ATPP**. These results clearly indicated that photoinduced energy transfer from the anthraquinone moiety to the porphyrin moiety occurred [1,29] in the dyad **4** (Fig. 4, inset).

3.3.2. Excitation on the porphyrin moiety

Fluorescence emission spectra of compound **2** and the dyads (**3** and **4**) in CH_2Cl_2 excited at 420 nm are shown in Fig. 5. The fluorescence intensity of compound **2** was calculated as 90% in comparison with the fluorescence intensity of original porphyrin **ATPP** at equal concentration. However the fluorescence quenching efficiency of porphyrin in the dyad **3** and **4** was found as 43% and 49% respectively. This could be explained by the introduction of the anthraquinone group as the electron acceptor, resulting in the photoinduced intramolecular electron transfer from the excited porphyrin to the appended anthraquinone moiety [1,29,30]. This could be further confirmed by the observation of the charge-separated state of dyads through the followed transient absorption spectra [1].

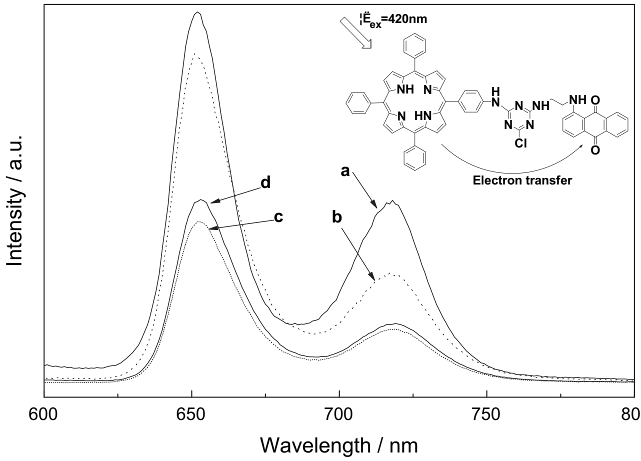
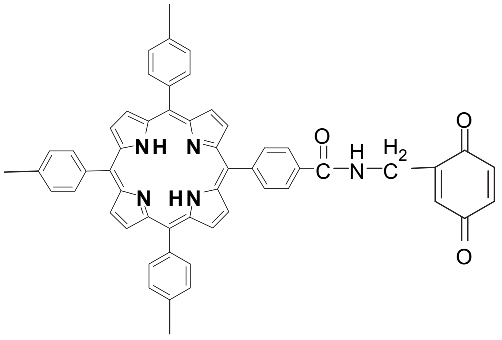


Fig. 5. Fluorescence emission spectra of (a) **ATPP**, (b) porphyrin-anthraquinone dyad **2**, (c) porphyrin-anthraquinone dyad **3**, and (d) porphyrin-anthraquinone dyad **4** in dichloromethane. The concentrations were held constant to 5×10^{-6} mol/L for all of the species. $\lambda_{ex} = 420$ nm.

Transient absorption spectra observed at 0–20 μs after laser pulse irradiation for a deoxygenated dichloromethane solution of the original porphyrin **ATPP,** compound **1** and the porphyrin-anthraquinone dyads **3**, **4** is shown in Fig. 6. Compound **1**, similar to **ATPP**, exhibits absorption peaks at 450 nm, 540 nm, 570 nm, 620 nm, 675 nm and 780 nm, which are assigned to the triplet excited state of porphyrin (Fig. 6a and b) [27,31]. In the transient absorption spectrum of the dyads **3** at 2 μs, the absorption intensity of triplet (peaks at 460 570, and 780 nm) decayed quickly; simultaneously a new band corresponding to the porphyrin cation radical ($H_2P^{\bullet+}$) appeared at 600 nm and 650 nm (Fig. 6c). This indicated that, in the dyad **3**, the electron transfer occurred from the porphyrin moiety to the anthraquinone moiety [1,28,32].

The absorption intensity of the transient product of dyad **3** at 650 nm are fitted according to the first-order exponential decay function, $I = I_0 + A * e^{-t/\tau}$, in which the τ is the lifetime of transient product. Results show that the lifetime and the decay rate constant $k(k = 1/\tau)$ of the porphyrin cation radical ($H_2P^{\bullet+}$) in the dyad **3** were 1.42 μs and $7.04 \times 10^5\ s^{-1}$ respectively (Fig. 7). Herein the *k* value is smaller than that obtained from the simple porphyrin-quinone (compound **5**) with an amide linker reported in the literature [4]. Thus a faster transfer reaction occurs in the dyad **3** than in the simple porphyrin-quinone [4], indicating that the anthraquinone might be a better acceptor than the simple parent quinone group for the porphyrin compounds.



Similar results were obtained with dyad **4** and the lifetime of the charge-separated state $H_2P^{\bullet+}–EQ^{\bullet-}$ was determined as 1.33 μs (Fig. 6d).

3.4. Energy level diagram of the anthraquinone-porphyrin dyads

Electrochemical studies using cyclic voltammetry were performed to arrive at the redox potentials of the investigated compounds. Compound **1** exhibited four one-electron redox processes at $E_{1/2} = 0.76$ V, 1.08 V, −1.53 V, and −1.86 V vs Ag/Ag^+ (Fig. 8a), corresponding to the redox of the ground-state porphyrin ring. All of the peak–peak separation values of the redox peaks are larger than 59 mV, therefore, they are quasi-reversible redox processes [33]. In the dyad **4**, the oxidation processes were irreversible (Fig. 8b). The first and second oxidation of the ground-state porphyrin ring were located at $E_{pa} = 0.77$ V and 1.19 V vs Ag/Ag^+ respectively. Two one-electron reversible processes at $E_{1/2} = -1.52$ V and −1.81 V were also observed, corresponding to the reduction of the porphyrin ring. Further, additional reversible reduction of the ground-state anthraquinone was also observed at $E_{1/2} = -1.23$ V vs Ag/Ag^+ under the experimental conditions. From the electrochemical data coupled with the absorption and emission spectra, an energy-level diagram (Fig. 9) could be constructed to explain the different photochemical events observed.

The triplet state energy of a tetraphenyl porphyrin free base (H_2P) was cited from the literature [29]. The free-energy change for

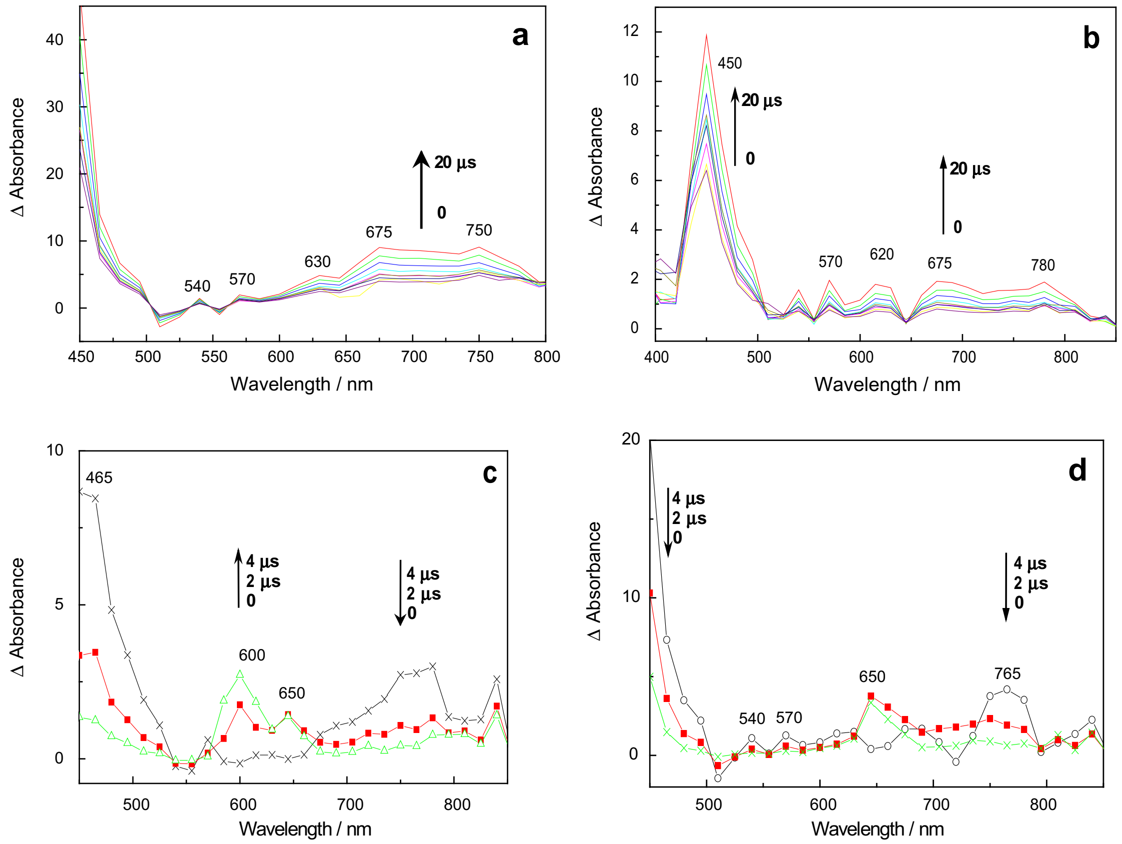


Fig. 6. Transient absorption spectra of (a) **ATPP**, (b) Compound **1**, (c) porphyrin-anthraquinone dyad **3**, and (d) porphyrin-anthraquinone dyad **4** at different times after the 532 nm laser irradiation in **N_2**-saturated dichloromethane. The concentrations were held at 5 × 10^{-6} mol/L.

the singlet energy transfer (G_{ENT}, the energy difference between the excited singlet state of anthraquinone and that of porphyrin as evaluated from the fluorescence peaks) was calculated as −2.15 eV. This is the driving force for the occurrence of energy transfer from the excited anthraquinone moiety to the excited porphyrin moiety. It was calculated that the LUMO of the porphyrin moiety (−3.20 eV) is higher than that of the anthraquinone moiety (−3.47 eV). Hence the electron would be unlikely to transfer from the anthraquinone moiety to the porphyrin moiety. The driving force for the electron transfer process from the excited porphyrin moiety to the anthraquinone moiety is the free-energy change of charge separation (ΔG_{CS}), which was calculated as −0.34 eV from the Weller equation [34]. The relatively low quantum yield of 42% for the process could also been explained because of such a low ΔG_{CS}(−0.34 eV). Upon excitation of porphyrin in the dyad **4**, the major process

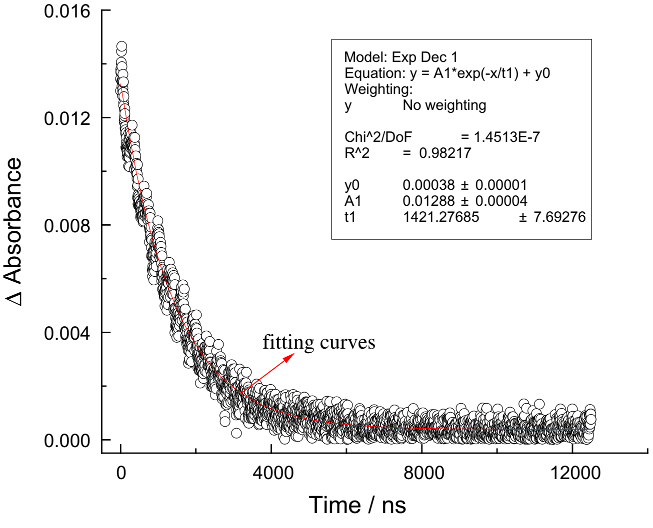


Fig. 7. Time resolved absorption-time-profile of porphyrin-anthraquinone dyad **3** at 650 nm in **N_2**-saturated dichloromethane.

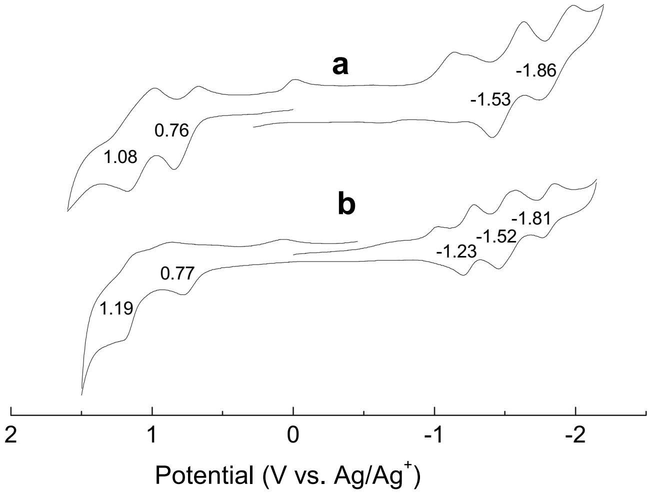


Fig. 8. Cyclic voltammogram of (a) compound **1**, and (b) porphyrin-anthraquinone dyad **4** in dichloromethane, 0.05 mol/L **$TBAPF_6$**. Scan rate = 100 mV/s.

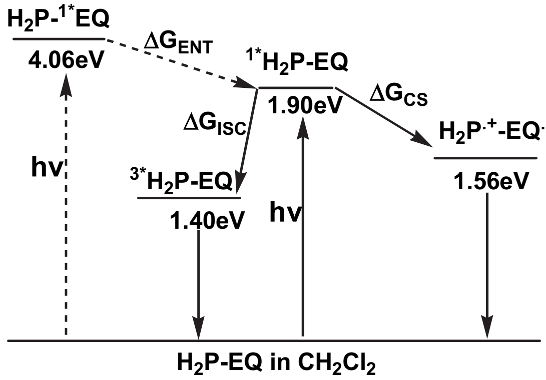


Fig. 9. Energy level diagram showing the different photochemical events of the **H_2P–EQ** dyads in dichloromethane after excitation of the porphyrin moiety (–) or the anthraquinone moiety (…).

involves charge separation from $^{1*}H_2P$ to form $H_2P^{\cdot+}$–$EQ^{\cdot-}$ because of the appropriate exothermic conditions, resulting in the fluorescence quenching of porphyrin moiety. The energy-level diagram of dyad **3** is similar.

4. Conclusions

In conclusion, the porphyrin-anthraquinone dyads linked by a triazine group were successfully shown to be a model photosynthetic reaction center to simulate the electron transfer from chlorophylls to the electron acceptors. In the ground state, there is no appreciable interaction between porphyrin moiety and anthraquinone moiety in the dyads. But, efficient photoinduced energy transfer from the singlet excited anthraquinone to the porphyrin as well as the photoinduced electron transfer from the singlet porphyrin to the anthraquinone entity was observed in the dyads, resulting in the formation of the charge-separated state $H_2P^{\cdot+}$–$EQ^{\cdot-}$. The lifetime of the charge-separated state was found as long as 1.42 and 1.33 μs for dyads **3** and **4** respectively.

Acknowledgments

The authors would like to thank Prof. XiaoJun Peng from Dalian University of Technology for the assistance in the cyclic voltammogram technique and the measurements of transient absorption spectra.

References

[1] D'Souza F, Smith PM, Zandler ME, McCarty AL, Itou M, Araki Y, et al. Energy transfer followed by electron transfer in a supramolecular triad composed of boron dipyrrin, zinc porphyrin, and fullerene: a model for the photosynthetic antenna-reaction center complex. Journal of American Chemical Society 2004;126:7898–907.
[2] Balzani V, Bolletta F, Gandolfi MT, Maestri M. Bimolecular electron transfer reactions of the excited states of transition metal complexes. Topics in Current Chemistry 1978;75:1–64.
[3] Wiehe A, Senge MO, Schäfer A, Speck M, Tannert S, Kurreck H, et al. Electron donor-acceptor compounds: exploiting the triptycene geometry for the synthesis of porphyrin quinone diads, triads, and a tetrad. Tetrahedron 2001;57:10089–110.
[4] Schmidt JA, McIntosh AR, Weedon AC, Bolton JR, Connolly JS, Hurley JK, et al. Intramolecular photochemical electron transfer. 4. Singlet and triplet mechanisms of electron transfer in a covalently linked porphyrin-amide-quinone molecule. Journal of American Chemical Society 1988;110:1733–40.
[5] Kong JLY, Loach RA. Syntheses of covalently-linked porphyrin-quinone complexes. Journal of Heterocyclic Chemistry 1980;17:737–44.
[6] Tabushi I, Koga N, Yanagita M. Efficient intramolecular quenching and electron transfer in tetraphenyl-porphyrin attached with benzoquinone or hydroquinone as a photosystem model. Tetrahedron Letters 1979;20:257–60.
[7] Khundkar LR, Perry JW, Hanson JE, Dervan PB. Weak temperature dependence of electron transfer rates in fixed-distance porphyrin-quinone model systems. Journal of American Chemistry Society 1994;116:9700–9.
[8] Sakata Y, Imahori H, Tsue H, Higashida S, Akiyama T, Yoshizawa E, et al. Control of electron transfer and its utilization. Pure and Applied Chemistry 1997;69:1951–6.
[9] D'Souza F, Gadde S, Zandler ME, Arkady K, El-Khouly ME, Fujitsuka M, et al. Studies on covalently linked porphyrin-C_{60} dyads: stabilization of charge-separated states by axial coordination. Journal of Physical Chemistry A 2002;106:12393–404.
[10] Gust D, Moore TA, Moore AL, Lee SJ, Bittersmann E, Luttrull DK, et al. Efficient multistep photoinitiated electron transfer in a molecular pentad. Science 1990;248:199–201.
[11] Jing BW, Zhu DB. Fullerene–fluorescein–anthracene hybrids: a model for artificial photosynthesis and solar energy conversion. Tetrahedron Letters 2004;45:221–4.
[12] Siemiarczuk A, McIntosh AR, Ho TF, Stillman MJ, Roach KJ, Weedon AC, et al. Intramolecular photochemical electron transfer. 2. Fluorescence studies of linked porphyrin-quinone compounds. Journal of American Chemistry Society 1983;105:7224–30.
[13] Fajer J, Barkigia KM, Melamed D, Sweet RM, Kurreck H, Gersdorff JV, et al. Molecular structures of porphyrin-quinone models for electron transfer. Journal of Physical Chemistry 1996;100:14236–9.
[14] Okamoto K, Fukuzumi S. Hydrogen bonds not only provide a structural scaffold to assemble donor and acceptor moieties of zinc porphyrin-quinone dyads but also control the photoinduced electron transfer to afford the long-lived charge-separated states. Journal of Physical Chemistry B 2005;109:7713–23.
[15] Wilford JH, Archer MD, Bolton JR, Ho TF, Schmidt JA, Weedon AC. Redox potentials of some covalently linked porphyrin-quinones and related molecules. Journal of Physical Chemistry 1985;89:5395–8.
[16] Kamioka K, Cormier RA, Lutton TW, Connolly JS. Charge-transfer emission in meso-linked zinc porphyrin-anthraquinone molecules. Journal of Amerian Chemistry Society 1992;114:4414–5.
[17] Imahori H, Tamaki K, Yamada H, Yamada K, Sakata Y, Nishimura Y, et al. Photosynthetic electron transfer using fullerenes as novel acceptors. Carbon 2000;38:1599–605.
[18] Schuster DI, MacMahon S, Guldi DM, Echegoyen L, Braslavsky SE. Synthesis and photophysics of porphyrin–fullerene donor–acceptor dyads with conformationally flexible linkers. Tetrahedron 2006;62:1928–36.
[19] Shibano Y, Sasaki M, Tsuji H, Araki Y, Ito O, Tamao K. Conformation effect of oligosilane linker on photoinduced electron transfer of tetrasilane-linked zinc porphyrin–[60]fullerene dyads. Journal of Organometallic Chemistry 2007; 692:356–67.
[20] Marcus RA. Electron transfer reactions in chemistry: theory and experiment (Nobel lecture). Angewandate Chemie. International Edition in English 1993;32:1111–21.
[21] Tao ML, Liu DZ, Zhang MH, Zhou XQ. Photoinduced energy and electron transfer in porphyrin-oxadiazole dyads. Acta Chimica Sinica 2008;66:1252–8. in Chinese.
[22] Wang XQ, Wang CX, Wang QM, Yu LX, Cao XZh, Min ChZ, et al. A study of intramolecular electron transfer process of porphyrin—anthraquinone under photoinduction(I). Chemical Journal of Chinese University 1997;18:834–9.
[23] Luguya R, Jaquinod L, Fronczek FR, Vicente MGH, Smith KM. Synthesis and reactions of meso-(p-nitrophenyl)porphyrins. Tetrahedron 2004;60:2757–63.
[24] Armarego WLF, Chaj CLL. Purification of laboratory chemicals. 5th ed., 2002. p. 215.
[25] Wan Y, Alterman M, Larhed M, Hallberg A. Dimethylformamide as a carbon monoxide source in fast palladium-catalyzed aminocarbonylations of aryl bromides. Journal of Organic Chemistry 2002;67:6232.
[26] Sun WH, Yin JM, Gao DB, Zhou GY, Zheng XF. Dimethylformamide as carbon monoxide source in photoassisted hydroesterification of olefins. Chinese Journal of Catalysis 2004;25:481–4.
[27] Rodriguez J, Kirmaier C, Holten D. Optical properties of metalloporphyrin excited states. Journal of American Chemistry Society 1989;111:6500–6.
[28] Fukuzumi S, Endo Y, Kashiwagi Y, Araki Y, Ito O, Imahori H. Novel photocatalytic function of porphyrin-modified gold nanoclusters in comparision with the reference porphyrin compound. Journal of Physical Chemistry B 2003;107:11979–86.
[29] Sirish M, Maiya BG. Fluorescence studies on a supramolecular porphyrin bearing anthrance donor moieties. Journal of Photochemistry and Photobiology A: Chemistry 1995;85:127–35.
[30] Macpherson AN, Liddell PA, Lin S, Noss L, Seely GR, DeGraziano JM, et al. Ultrafast photoinduced electron transfer in rigid porphyrin-quinone dyads. Journal of American Chemistry Society 1995;117:7202–12.
[31] Luo C, Guldi DM, Imahori H, Tamaki K, Sakata Y. Sequential energy and electron transfer in an artificial reaction center: formation of a long-lived charge-separated state. Journal of American Chemistry Society 2000;122:6535–51.
[32] Imahori H, Liu JC, Hotta H, Kira A, Umeyama T, Matano Y, et al. Hydrogen bonding effects on the surface structure and photoelectrochemical properties of nanostructured SnO_2 electrodes modified with porphyrin and fullerene composites. Journal of Physical Chemistry 2005;109:18465–74.
[33] Wang J, editor. Analytical electrochemistry. 2nd ed. John Wiley & Sons, Inc; 2000. p. 31–3.
[34] Rehm D, Weller A. Kinetics of fluorescence quenching by electron and hydrogen-atom transfer. Israel Journal of Chemistry 1970;8:259–71.