Asian Journal of Chemistry; Vol. 24, No. 8 (2012), 3490-3492

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Synthesis, Photophysical and Electochemical Properties of Amide-bridged Porphyrin-Anthraquinone Dimers

LI-ZENG LIU[1,2], DONG-ZHI LIU[1], MIN-LI TAO[1], XUE-QIN ZHOU[1] and WEI LI[1,*]

[1]School of Chemical Engineering, Tianjin University, Tianjin 300072, P.R. China
[2]College of Science, Tianjin University of Commerce, Tianjin 300134, P.R. China

*Corresponding author: Fax: +86 22 27400911; Tel: +86 22 27400911; E-mail: zhouxueqin@tju.edu.cn; liulizeng@126.com

(*Received*: 18 July 2011; *Accepted*: 12 March 2012) AJC-11173

Photoinduced electron-transfer processes of two newly synthesized porphyrin-anthraquinone dyads bridged with amide were studied with the UV-visible, fluorescence and transient absorption spectra. Results indicated that the intramolecular electron-transfer might take place *via* the excited states of the 5-(4-carboxyphenyl)-10,15,20-triphenylporphyrin unit to the anthraquinone moiety.

Key Words: Porphyrin, Anthraquinone, Electron transfer, Dyads, Synthesis.

INTRODUCTION

Studies on covalently linked donor-acceptor dyads are of current interest because of their potential applications in photovoltaic devices and photosynthesis to mimic the primary events of photosynthetic reaction centers[1-3]. Photophysical properties of a number of dyes (porphyrins[4,5], phthalocyanines[6,7] subphthalocyanines[8,9]) have been studied in an attempt to find correlation between the molecular structure of the dye and its ability to generate a photoinduced electron transfer. Among these, porphyrin derivatives have been extensively studied due to their similar structure with the natural photoreaction center[10]. Anthraquinone and its derivations as the electron acceptor in these dyads are also appealing because of excellent electron acceptor property[11,12] as well as their similar structure to the quinone acceptors Q_A and Q_B in natural photosynthesis systems[10]. In this article we report the synthesis of dyads with porphyrin as the donor, anthraquinone as the acceptor and amide groups as the linker (Fig. 1). The absorption spectra, steady-state fluorescence spectra and nanosecond transient absorption spectra were measured to investigate the possible intramolecular electron transfer, thus to evaluate the potential applications of these dyads.

EXPERIMENTAL

5-(4-Carboxyphenyl)-10,15,20-triphenylporphyrin (CTPP) was synthesized by a modification of a procedure by

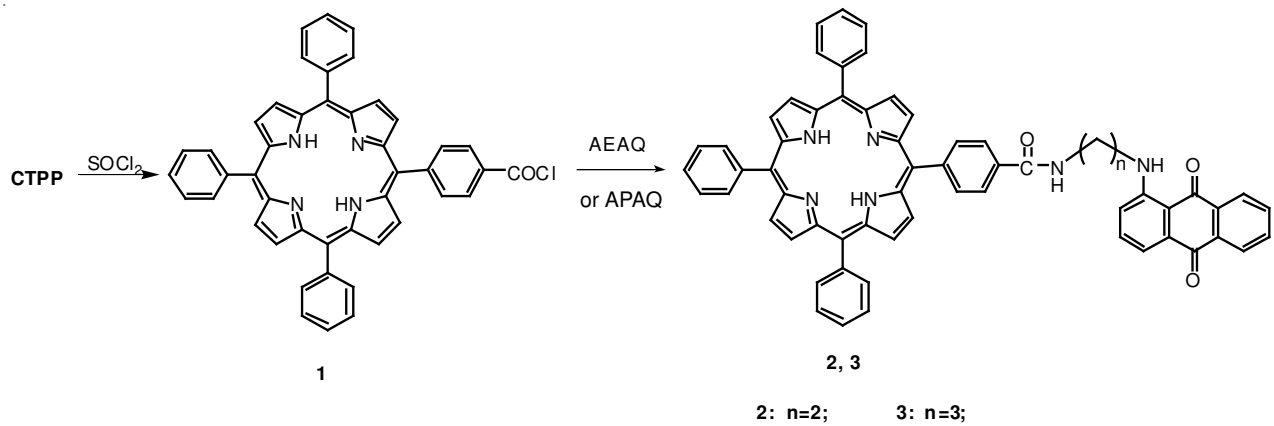

Fig. 1. Synthesis of compound **2** and **3**

Vermathen and co-workers[11]; details of the synthesis are given in the preparation section. Synthesis and purification of aminoethyl amino-anthraquinone (AEAQ) and aminopropyl amino-anthraquinone (APAQ) were carried out according to a modification of a literature methods[12]; CH_2Cl_2 were purified by according to the standard methods[13]. All other reagents were of analytical grade and used without further purification unless otherwise indicated. Infrared spectra were recorded on a BIO-RAD FTS3000 IR spectrometer; mass spectra were recorded on a VG ZAB-HS mass spectrometer; ^{1}H NMR spectra were measured on Varian, Unity-Plus 400 NMR instrument, in $CDCl_3$; fluorescence spectra were recorded on a Varian CARY ECLIPSE fluorospectrophotometer; electronic absorption spectra were recorded on a Thermo Spectronic, UVG105130 UV-visible spectrometer. Transient absorption measurements were carried out on a LP920 Laser Flash photolysis spectrometer, with laser Nd:YAG as the excitation source, excitation wavelength of 532 nm, pulse width of 10 ns.

Preparation of 5-(4-carboxyphenyl)-10,15,20-triphenylporphyrin (CTPP): The mixture of benzaldehyde (8.48 g, 0.08 mol) and carboxybenzaldehyde acid (3 g, 0.02 mol) in 200 mL of propionic acid was rapidly heated to reflux and pyrrole (5.5 mL, 0.08 mol) dissolved in 10 mL propionic acid was added to the mixture in 20 min. The reaction mixture was refluxed for 1 h. Petroleum ether (150 mL) was added to the suspension and then filtered to remove the tar. The filtrate was concentrated and extracted with dichloromethane. The extract was evaporated. The crude product dissolved in chloroform was chromatographed on silica gel with chloroform:ethyl acetate = 10:1 (v:v) to give the blue-purple solid product 60 mg, yield 4.9 %. ^{1}H NMR ($CDCl_3$), δ: 8.58-8.89 (m, 8H, C_4H_5N β-H), 8.23-7.44 (m, 16H,-C_6H_5), -2.87 (s, 2H, NH); ESI-MS (m/z): 659.4 $[M + 1]^+$.

Preparation of aminoethyl amino-anthraquinone (AEAQ): The mixture of 1-chloroanthraquinone (5 g, 0.02 mol) and 1,2-ethanediamine (5.67 mL ,0.085 mol) in 180 mL toluene was refluxed for 18 h. The cooled reaction mixture was concentrated by rotary evaporation and redissolved in methylene chloride, washed with H_2O to give the crude material. The organic layer was washed with water and extracted with 0.5 M HCl solution.The pH of water layer was adjusted to 7-8 with 10 % aqueous NaOH solution, extracted with CH_2Cl_2 and dried over $MgSO_4$. The solvent was evaporated to dryness to give red solid material 4.5 g, yield 80 %. ESI-MS (m/z): 267.2 $[M + 1]^+$.

Preparation of aminopropyl amino-anthraquinone (APAQ): The mixture of 1-chloroanthraquinone (5 g, 0.02 mol) and 1,3-propanediamine (7 mL, 0.085 mol) in 180 mL toluene was refluxed for 18 h. Purification by the procedures of the AEAQ to afforded 4.9 g of the title compound APAQ as a red solid material with a yield of 85 %. ESI-MS (m / z): 281 $[M + 1]^+$.

Preparation of porphyrin-anthraquinone dyads: The mixture of CTPP (33 mg, 0.05 mol), thionyl chloride (5 mL, 0.069 mol) in 15 mL chloroform was refluxed for 12 h. Then the solvent and excessive thionyl chloride was removed by rotary evaporation. The intermediate product was dissolved in 10 mL of dichloromethane and directly used to the next step reaction without further purification.

The mixture of AEAQ or APAQ (0.075 mol), triethylamine (5 mg, 0.05 mol) in 10 mL dichloromethane was cooled to 0 ºC and then the above intermediate product were added by dropping to the mixture. The reaction was kept at room temperature for 50 min. The solvent was evaporated. Purification of the crude product was accomplished by using column chromatography (dichloromethane:ethyl acetate = 30:1(v:v)) on silica gel to afforded CTPP-AEAQ dimers or CTPP-APAQ dimers.

Dyad 2: Blue-purple solid product, 18 mg, R_f = 0.6 (dichloromethane:ethyl acetate = 30:1 (v:v)), yield 39.5 %. IR (KBr, Δ, cm^{-1}): 3321 (N-H), 1731, 1713, 1665 ν(C=O), 1271 ν(N-H), 3055 ν(CH), 2924, 2853 ν(CH_2), 965 (porphyrin), 1505, 1630 ν(C=C); ^{1}H NMR ($CDCl_3$) δ: 9.96 (s, 1H, CONH), 8.85-8.75 (m, 8H, C_4H_5N β-H), 8.58-7.94 (m, 12H, ArH), 7.76-7.52 (m, 14H, ArH), 6.84 (s, 1H, ArNH), 3.86-3.84(d, *J* = 6.0 Hz, 2H, $CONHCH_2CH_2$), 3.72-3.71 (d, *J* = 5.6 Hz, 2H, $CONHCH_2CH_2$), -2.79 (s, 1H, NH), -2.88 (s, 1H, NH); FAB-MS (m/z): 908.1 $[M + 1]^+$.

Dyad 3: Blue-purple solid product, 20 mg, R_f = 0.7 (dichloromethane:ethyl acetate = 30:1 (v:v)), yield 43.3 %. ^{1}H NMR ($CDCl_3$), δ: 9.89 (s, 1H, CONH), 8.95-8.74 (m, 8H, C_4H_5N β-H), 8.26-8.09 (m, 11H, ArH), 7.79-7.73 (d, 11H, ArH), 7.64-7.55 (m, 4H, ArH), 6.74 (s, 1H, ArNH), 3.79-3.78 (d, *J* = 5.6 Hz, 2H), 3.57-3.56 (d, *J* = 5.6 Hz, 4H), -2.79 (s, 1H, NH), -2.88 (s, 1H, NH); FAB-MS (m/z): 921.0 $[M + 1]^+$.

RESULTS AND DISCUSSION

Synthesis: CTPP, AEAQ and APAQ were synthesized according to the literature procedures[11,12]. There are two main methods applied for synthesis of amides: (1) The acyl chlorides react with amines to obtain amides, (2) the condensation between carboxylic acids and amines. We tried to prepare dyad **2** and **3** by condensing CTPP and amino anthraquinone (AEAQ and APAQ) in which DCC was used as condensing agent. But this procedure requires a longer reaction time and gives a poor yield. The acyl chloride as an intermediate was a suitable way to get the target molecule, in which every reaction proceeded smoothly with a good or moderate yield of the target product.

UV-VIS spectral studies: UV-VIS spectroscopy is a simple method to determine the presence of ground-state interactions between the moieties in the dyads. The Soret and Q-bands of the porphyrin moiety appear at 414, 514, 547, 590 and 646 nm, respectively. The absorption peaks of dyad **3** locate at 420, 518, 550, 593 and 648 nm, which is similar to that of 10,15,20-triphenylporphyrin. These indicate that there is no appreciable electronic interaction between the CTPP moiety and the amino anthraquinone moiety in their ground states[14,15]. Similar results were also obtained from the absorption spectra of dyad **2**.

Fluorescence studies: The fluorescence spectra (Fig. 2) were determined at an excitation wavelength of 420 nm, where the porphyrin was exclusively excited. When the excitation wavelength was set at 420 nm, the fluorescence spectra of dyad **2** and **3** showed emission bands at γ = 625-780 nm. The fluorescence intensity of the CTPP moiety at 625-780 nm decreased 31.1 % for compound **3** and 37.1 % for dyad **2**, compared with that of 10,15,20-triphenylporphyrin in CH_2Cl_2. This could be explained by the photoinduced intramolecular electron

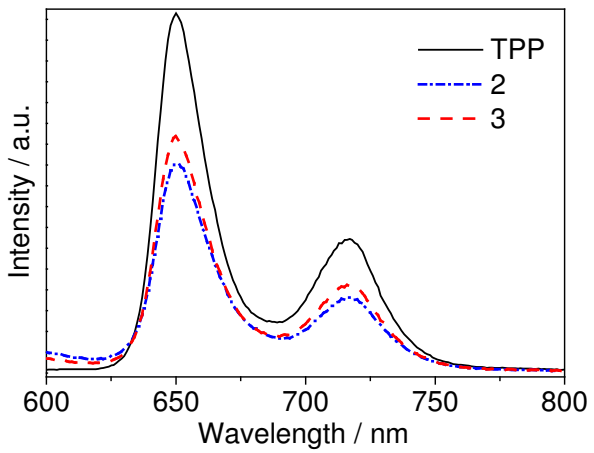

Fig. 2. Emission spectra of porphyrin-anthraquinone compounds connected with amide bond. The concentrations of compounds were maintained at 5×10^{-6} mol/L in CH_2Cl_2, λ_{ex} = 420 nm

transfer from the excited porphyrin to the appended anthraquinone moiety, which has been reported in porphyrin-anthraquinone dyads with different linkers[16-18].

Nanosecond transient absorption spectral studies: The nanosecond transient absorption spectra of CTPP, dyad **2** and dyad **3** in deaerated CH_2Cl_2 were obtained with the excitation of 532 nm laser and results are shown in Fig 3. CTPP exhibits the absorption bands at 540, 570, 630, 690 and 780 nm at 2 μs after the laser pulse excitation. These are assigned to the triplet excited state of porphyrins[18,19]. Similar absorption peaks were found with dyad 2 and 3 (540, 570, 630, 690 and 780 nm), which are also attributed to the triplet excited state of porphyrins. No new bands were observed during the experiments to indicate the exist of the porphyrin cation radical ($TPP^{\cdot+}$). This might be because that the lifetime of the charge -separated state [$TPP^{\cdot+}$ – $AQ^{\cdot-}$] is too short to be detected in our experiments.

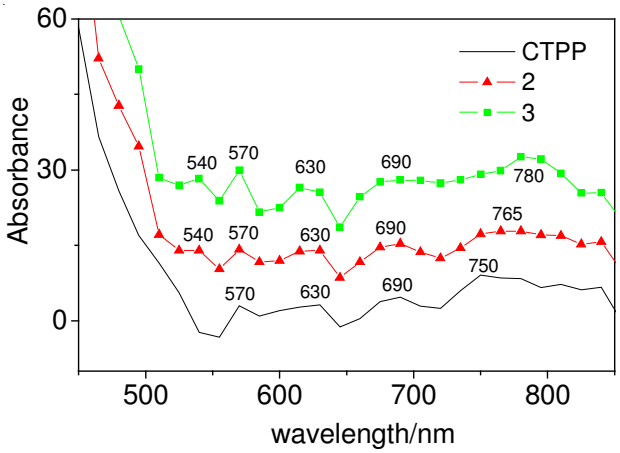

Fig. 3. Transient absorption spectra of CTPP, compound **2**, compound **3** at 2 μs after 532 nm laser irradiation in N_2-saturated dichloromethane. The concentrations were maintained at 5×10^{-6} mol/L

Conclusion

Two amide-linked porphyrin-anthraquinone dyads were synthesized and shown to be a model photosynthetic reaction center to simulate the electron transfer between chlorophylls and the electron acceptors. The fluorescence quenching is attributed to the intramolecular electron-transfer interaction from the porphyrin moiety to the anthraquinone unit. Nanosecond scale transient absorption spectra did not give any evidence of charge-separation. The simply synthesis route used to obtain donor-acceptor photoinduced models is worthy of note.

ACKNOWLEDGEMENTS

The authors acknowledged the National Nature Sciences Foundation of China (No. 20976122) and the Tianjin Univeristy of Commerce (No. 090114) for financial supports.

REFERENCES

1. Y. Shibano, M. Sasaki, H. Tsuji, Y. Araki, O. Ito and K. Tamao, *J. Organomet. Chem.*, **692**, 356 (2007).
2. J. Baffreau, S. Leroy-Lhez, N.V. Anh, R.M. Williams and P. Hudhomme, *Chem. Eur. J.*, **14**, 4974 (2008).
3. B.W. Jing and D.B. Zhu, *Tetrahedron Lett.*, **45**, 221 (2004).
4. F. D'Souza, G.R. Deviprasad, M.E. Zandler, M.E. El-Khouly, M. Fujitsuka and O. Ito, *J. Phys. Chem. B*, **106**, 4952 (2002).
5. D. Baskaran, J.W. Mays, X.P. Zhang and M.S. Bratcher, *J. Am. Chem. Soc.*, **127**, 6916 (2005).
6. H.X. Luo, M. Fujitsuka, O. Ito and M. Kimura, *J. Photochem. Photobiol. A: Chem.*, **156**, 31 (2003).
7. J. Ranta, T. Kumpulainen, H. Lemmetyinen and A. Efimov, *Org. Chem.*, **75**, 5178 (2010).
8. B.D. Rey, U. Keller, T. Torres, G. Rojo, F. Agulló-López, S. Nonell, C. Martí, S. Brasselet, I. Ledoux and J. Zyss, *J. Am. Chem. Soc.*, **120**, 12808 (1998).
9. C.G. Claessens, D. González-Rodríguez, R.S. Iglesias and T. Torres, *C.R. Chimie*, **9**, 1094 (2006).
10. W. Lubitz, F. Lendzian and R. Bittl, *Acc. Chem. Res.*, **35**, 313 (2002).
11. M. Vermathen, E.A. Louie, A.B. Chodosh, S. Ried and U. Simonis, *Langmuir*, **16**, 210 (2000).
12. X.Q. Wang, C.X. Wang, Q.M. Wang, L.X. Yu, X.Zh. Cao, Ch.Z. Min and L.P. Wang, *Chem. J. Chin. Univ.*, **18**, 834 (1997).
13. D.D. Perrin and W.L. F. Armarego, In Purification of Laboratory Chemicals, Pergamon Press: New York (1988).
14. H.P. Zeng, T.T. Wang, A.S.D. Sandanayaka, Y. Araki and O. Ito, *J. Phys. Chem. A*, **109**, 4713 (2005).
15. W. Xu, H.L. Chen, Y.F. Wang, Ch.T. Zhao, X.Y. Li, Sh.Q. Wang and Y.X. Weng, *Chem. Phys. Chem.*, **9**, 1409 (2008).
16. M.L. Tao, L.Z. Liu, D.Zh. Liu and X.Q. Zhou, *Dyes Pigm.*, **85**, 21 (2010).
17. M. Sirish and B.G. Maiya, *J. Photochem. Photobio. A: Chem.*, **85**, 127 (1995).
18. A.N. Macpherson, P.A. Liddell, S. Lin, L. Noss, G.R. Seely and J.M. DeGraziano, *J. Am. Chem. Soc.*, **117**, 7202 (1995).
19. J. Rodriguez, C. Kirmaier and D. Holten, *J. Am. Chem. Soc.*, **111**, 6500 (1989).