Triphenylamine as an Electron/Energy Donor in a Supramolecular Zinc Tetraphenylporphyrin System

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The supramolecular systems containing an electron acceptor, zinc 5,10,15,20-*meso*-tetraferrocenylporphyrin and a pyridine-based triphenylamine as an electron/energy donor, has been investigated. Fluorescence and transient fluorescence spectra revealed that the axial coordinative complex performed a intramolecular photoinduced electron/energy-transfer from the triphenylamine to the porphyrin unit (phene-based triphenylamine used as a reference). Pyridine/phene-based triphenylamine derivatives were synthesized and characterized by ^{1}H NMR, IR and ESI-MS.

Key Words: Synthesis, Zinc porphyrin, Triphenylamine, Electron/energy transfer, Dyads.

INTRODUCTION

Studies of the bacterial photosynthetic reaction centers have revealed that the electron/energy donor and acceptor entities are arranged through noncovalent incorporation into a well-defined protein matrix[1-4]. The light-induced electron transfer and energy transfer events occur between these well-organized pigments in the photosynthetic systems. The natural photosynthetic reaction center is too complex to reproduce synthetically. To develop relatively simple donor-acceptor model systems designed to mimic the events of the photosynthetic reaction center has been one of the important goals of chemistry during the past two decades[5-9]. Porphyrin is a suitable component owing to its resemblance to the natural photosynthetic chlorophyll pigment[10]. Zinc porphyrin (ZnTPP) is able to complex with basic substances (such as pyridine), furthermore the resulting complexes are observed to be stable in certain circumstance. This type of complexing is of considerable biological importance[11]. Triphenylamines (TPA) are not a component of any natural photosynthetic system. However, triphenylamines have been found to be a potential donor in modeling photosynthetic systems[12]. Here, a pyridine-appended triphenylamine has been chosen to form stable coordination bonds with metal ions in the porphyrin cavity. Furthermore, the electron/energy-transfer efficiencies in TPA-ZnTPP have been systematically performed by using different methods such as (i) decrease in donor fluorescence intensity, (ii) increase in acceptor fluorescence intensity, and (iii) decrease in donor lifetime.

EXPERIMENTAL

The ZnTPP was synthesized by the method of Adler *et al.*[13]. Synthesis and purification of 4-[*N,N*-di(4-tolyl)amino]benzaldehyde(1) was carried out according to a modification of a literature methods[14]. All other reagents and solvents were reagent grade and further purified by the standard methods if necessary. ^{1}H NMR spectra were measured with a VARIAN UNITY INOVA 500 spectrometer. ESI mass spectra were obtained on a LCQ Advantage MAX mass spectrometer. Infrared spectra were recorded on a Bio-rad FTS3000. The absorption spectra were received using Thermo spectronic, Helios Gamma spectrometer in the range of 200-800 nm. Steady-state fluorescence spectra were obtained on a Varian CARY ECLIPSE fluorospectrophotometer. The time-resolved fluorescence decay measurements were carried out using a HORIBA Jobin Yvon IBH instrument based time correlated single-photon counting (TCSPC) fluorescence spectrometer. The solution was deaerated with N_2-bubbling before measurements.

Preparation of 4-[*N,N*-di-(4-tolyl)amino]benzaldehyde oxime (TPAOx): Compound **1** (0.15 g, 0.5 mmol), hydroxylamine hydrochloride (0.14 g, 2 mmol) and dichloromethane (50 mL) were mixed and stirred at 25 ºC for 6 h. The reaction mixture was concentrated and then purified by silica-gel column chromatography with petroleum ether/ethyl acetate as eluent. Yield: 0.13 g (82 %) light-yellow solid. ESI-MS (*m/z*): 317.1 [M+H]⁺. ^{1}H NMR (CDCl₃): δ, ppm 8.06 (s, 1H, -N = CH),
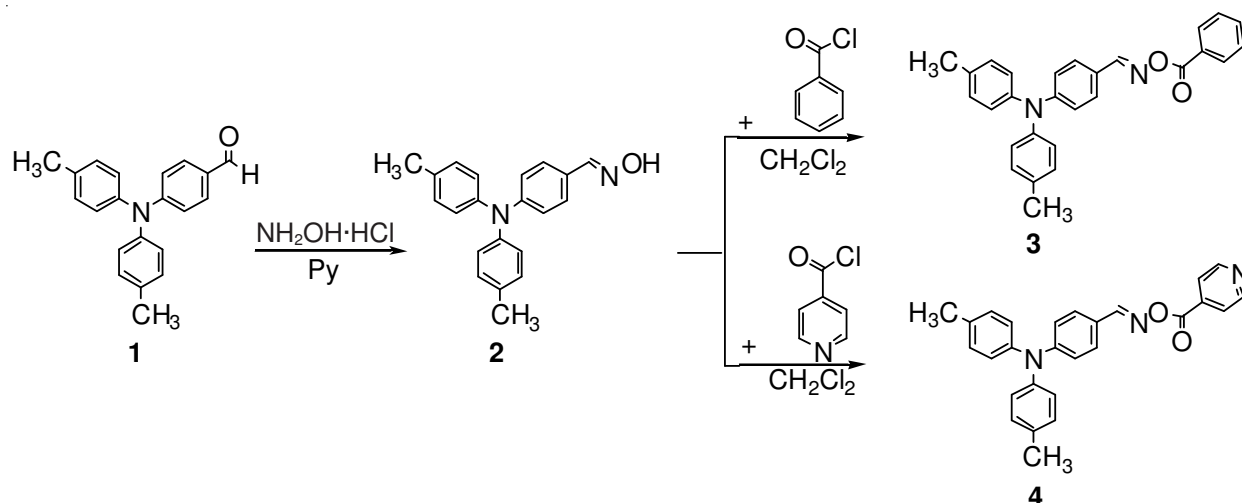
Fig. 1. Synthesis of compound **3** and **4**

7.38 (d, *J* = 5Hz, 2H, ArH), 7.09 (d, *J* = 5Hz, 4H, ArH), 7.02 (d, *J* = 5Hz, 4H, ArH), 6.97 (d, *J* = 5Hz, 2H, ArH), 2.33 (s, 6H, -CH$_3$).

Preparation of 4-[*N,N*-di-(4-tolyl)amino]benzaldehyde oxime *N-O*-benzoate (TPAOxPh): Benzoyl chloride (0.5 mL, 4 mmol), TPAOx (0.3 g, 1 mmol), triethylamine (1.2 mL, 8 mmol) and THF (40 mL) were stirred at 0 ºC overnight under nitrogen. Then the reaction mixture was poured into cold water and extracted with chloroform (3 × 80 mL). The combined organic layer was dried with anhydrous MgSO$_4$, filtered and dried. The crude product was then purified by silica-gel column chromatography with petroleum ether/dichloromethane as eluent. Yield: 0.28 g (67 %) light-green solid. ESI-MS (*m/z*): 420.9 [M+H]$^+$. IR (KBr, ν$_{max}$, cm^{-1}) : 2961, 2852 (γ$_{H-C=}$), 2921 (γ$_{-CH_3}$), 1914 (γ$_{C=N}$), 1744 (γ$_{C=O}$), 1596, 1505, 1464 (γ$_{C=C}$); ^{1}H NMR (CDCl$_3$): δ, ppm 8.14-7.56 (m, 5H, ArH), 8.44 (s, 1H, -N=CH), 8.13(d, *J* = 3.5 Hz, 2H, ArH), 7.49 (t, *J* = 8.0 Hz, 2H, ArH), 7.05 (d, *J* = 8.5Hz, 4H, ArH), 7.12 (d, *J* = 8.5 Hz, 4H, ArH), 2.35 (s, 6H, -CH$_3$).

Preparation of 4-[*N,N*-di-(4-tolyl)amino]benzaldehyde oxime *N-O*-isonicotinate (TPAOxPy): Isonicotinic acid (0.22 g, 1.8 mmol), thionyl chloride (0.4 mL, 5.6 mmol) in 15 mL chloroform were refluxed for 6 h. The reaction mixture was concentrated by rotary evaporation. Then to this intermediate mixture the pre-cooled mixture of TPAOx (0.3 g, 1 mmol), triethylamine (1.2 mL, 8 mmol) and 10 mL CH$_2$Cl$_2$ was slowly added in. The mixture was allowed to react for 2 h at room temperature. After removing the solvent, the crude product was dissolved in 5 mL CH$_2$Cl$_2$ and purified by column chromatography on silica gel with CH$_2$Cl$_2$: Methanol = 3:1 as eluent. Yield 84 %. ESI-MS (*m/z*): 422.1 [M +H]$^+$. IR (KBr, ν$_{max}$, cm^{-1}): 3209, 2851 (γ$_{H-C=}$), 2920 (γ$_{-CH_3}$), 1920 (γ$_{C=N}$), 1735 (γ$_{C=O}$), 1600, 1506, 1449 (γ$_{C=C}$); ^{1}H NMR (CDCl$_3$): δ, ppm 8.84 (q, *J* = 2.0 Hz, 2H, -C$_5$H$_4$N), 7.96 (q, *J* = 3.5 Hz, 2H, -C$_5$H$_4$N), 8.45 (s, 1H, -N=CH), 7.58 (d, *J* = 9.0 Hz, 2H, ArH), 6.97 (d, *J* = 8.5 Hz, 2H, ArH), 7.05 (d, *J* = 8.5 Hz,4H, ArH), 7.13 (d, *J* = 8.0 Hz, 4H, ArH), 2.35 (s, 6H, -CH$_3$).

RESULTS AND DISCUSSION

Synthesis and characterization: Compounds TPAOxPy and TPAOxPh were synthesized from *N,N*-di-(4-tolyl)

benzenamine (Fig. 1). Compound **1** was converted to oxime using hydroxylamine with a yield of 85 %. The oxime compound TPAOx was reacted with isonicotinic choloride to achieve the target compound TPAOxPy. Compound TPAOxPh, as a reference compound in this paper, was synthesized in the same way except that benzoyl choloride was used instead.

Steady-state absorption measurements: In the visible spectral region, the absorption spectrum of ZnTPP locates at 419 nm (soret band), 548 nm, 586 nm (Q-bands)[15]. It was reported that the ZnTPP complex bearing a fifth ligand exhibited the red shifts of the soret band and Q bands[16], which has earlier been taken as evidence for the coordination of pyridine to a ZnTPP[17]. Fig. 2 shows the absorption spectra change of ZnTPP in the presence of various concentrations of TPAOxPy in CH$_2$Cl$_2$. The Soret band at 420 nm first decreased in intensity and then increased with shift to 427 nm. In the Q band region, the peak at 554 nm decreased and a new peak appeared at 604 nm. The spectral patterns are similar to those of the five-coordinated zinc porphyrins, therefore, the reaction corresponds to the axial ligation of one TPAOxPy to the zinc(II) center[18].
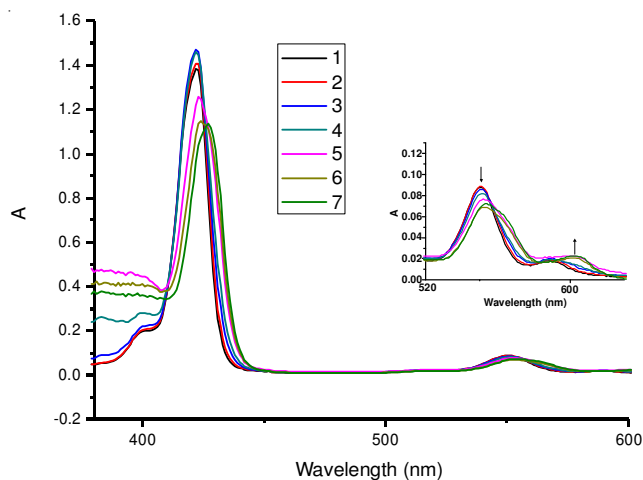

Fig. 2. Absorption spectral change of ZnTPP in CH$_2$Cl$_2$ in the presence of various concentrations of TPAOxPy. [TPAOxPy] = (1) 0M; (2) 4 × 10^{-6} M; (3) 4 × 10^{-5} M; (4) 8 × 10^{-5} M; (5) 2.4 × 10^{-4} M; (6) 3.2 × 10^{-4} M; (7) 4 × 10^{-4} M. The concentrations were maintained at 4 × 10^{-6} M for ZnTPP

Steady-state fluorescence spectra: The steady-state fluorescence emission spectra of ZnTPP, TPAOxPy and 1:1 complex of ZnTPP and TPAOxPy as well as those of the reference compound in CH₂Cl₂ are shown in Fig. 3. When excited at 371 nm, TPAOxPy shows a strong fluorescence emission at 460 nm and the characteristic emissions of ZnTPP at 580 nm, 650 nm also appeared. The presence of ZnTPP could quench the fluorescence of TPAOxPy and the larger concentration of ZnTPP brought about the larger fluorescence quantum yield, which was calculated as *ca.* 30.4 % (Fig. 3a). These results indicate that energy transfer and electron transfer might occur intermolecularly and intramolecularly in the TPAOxPy-ZnTPP 1:1 complex[19]. When the ZnTPP, ZnTPP-TPAOxPy were measured with excitation at 420 nm, which selectively excites the ZnTPP moiety, the fluorescence intensities of ZnTPP moiety were not significantly changed by the TPA moiety (Fig. 3b). Similar results were obtained with the mixture of days (ZnTPP + TPAOxPh). These results indicate that there is no photoinduced electron and energy transfer from the excited porphyrin to the intramolecular or intermolecular TPA moiety. For comparsion, the fluorescence emission spectra of mixtures of TPP (5,10,15,20-tetraphenyl porphyrin) with TPAOxPy and TPAOxPy in CH₂Cl₂ excited at 371, 420 and 550 nm were investigated. It is found that there is no change of the fluorescence emission spectra compared with the corresponding reference compound in these cases. This indirectly indicates that the electron/energy transfer in the coordinative complex at high dilutions may be of an intramolecular nature.
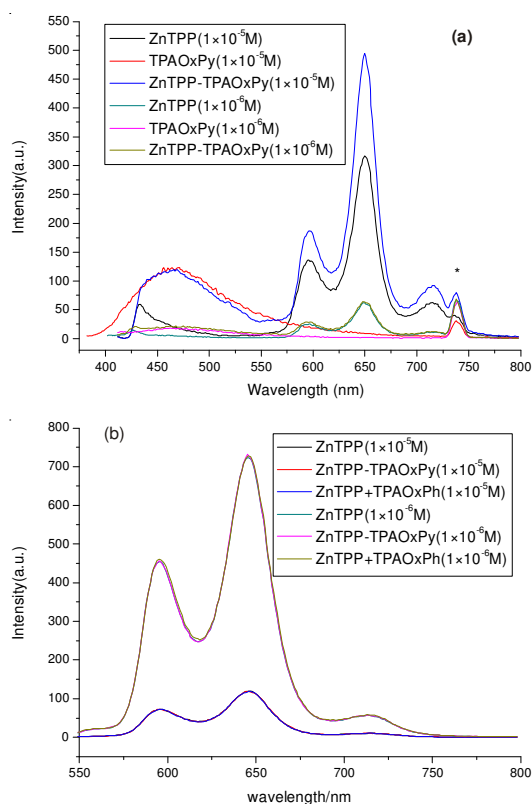
Transient fluorescence spectra: The fluorescence lifetimes (τ_f) of TPAOxPy, ZnTPP-TPAOxPy and ZnTPP +TPAOxPh were measured using a time-correlated single-photo-counting apparatus with excitation by specific Nanoled (Fig. 4). The fluorescence time profile of TPAOxPy excited at 339 nm were shown in Fig. 4a. The fluorescence lifetime of TPAOxPy was fitted to be 8.4 ns with a main component of 84.92 %. The ZnTPP-TPAOxPy excited at 339 nm was also fitted perfectly by biexponential fitting with a main component of 1.8 ns (50.87 %). The lifetime became shorter for TPAOxPy with zinc porphyrin, which clearly indicated that photoinduced energy/electron transfer from the TPAOxPy moiety to the porphyrin moiety occurred in the supramolecular system[20]. In Fig. 4b, the selective excitation of the ZnTPP moiety was carried out by 370 nm nanoled. The fit for the ZnTPP and the ZnTPP-TPAOxPy were fitted by biexponential fitting function with a main component of 1.7ns (91.68 %), 1.7ns (88.06 %) respectively. These results show that there is no photoinduced intramolecular electron and energy transfer from the excited porphyrin to the triphenylamine moiety. Compared with the ZnTPP-TPAOxPy dyads, the lifetime features of TPAOxPh and ZnTPP + TPAOxPh were measured at the same conditions as for TPAOxPy and ZnTPP-TPAOxPy. The fluorescence lifetime of TPAOxPh and the mixture of ZnTPP + TPAOxPh excited at 339 nm were 8.8ns (71.24 %), 8.6ns
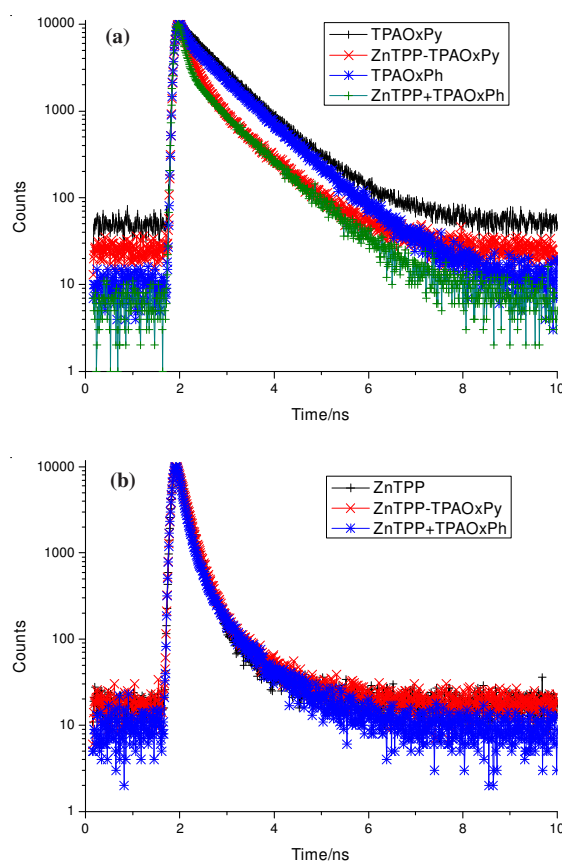

Fig. 3.   (a) Fluorescence spectra of ZnTPP, TPAOxPy and ZnTPP-TPAOxPy, λ_ex = 370 nm. (b) Fluorescence spectra of ZnTPP, ZnTPP-TPAOxPy and TPAOxPh + ZnTPP, λ_ex = 420 nm. All of the concentrations were maintained at 1 × 10⁻⁵ mol/L or 1 × 10⁻⁶ mol/L in CH₂Cl₂. (ZnTPP-TPAOxPy is the coordianted complex of TPAOxPy and ZnTPP, ZnTPP + TPAOxPh is the mixture of TPAOxPh and ZnTPP)

Fig. 4.   Fluorescence decay, as measured by nanosecond time correlated single photon counting. (a) Excitation by 339 nm nanoled, χ²_TPAOxPy = 1.1, χ²_ZnTPP-TPAOxPy = 1.1, χ²_TPAOxPh = 1.0, χ²_ZnTPP + TPAOxPh = 1.1; (b) Excitation by 370 nm nanoled, χ²_ZnTPP = 1.0, χ²_ZnTPP-TPAOxPy = 1.1, χ²_ZnTPP + TPAOxPh = 1.0. All of the concentrations were maintained at 4 × 10⁻⁶ mol/L in CH₂Cl₂. (χ² is a measure of mis-match between data and fitted function).

(52.06 %) respectively (Fig. 4a); the fluorescence lifetime of ZnTPP and the mixture of TPAOxPh and ZnTPP excited at 370 nm were 1.7 ns (91.68 %), 1.8 ns (50.26 %) respectively (Fig. 4b). The fluorescence lifetime of TPAOxPh and ZnTPP do not change with selectively excitation of the TPA unit or the TPP moiety, which indirectly indicated that photoinduced energy/electron transfer from the TPAOxPy moiety to the porphyrin moiety did not occurr in the intermolecular system[21]. In pyridine compound the TPAOxPy can come closer to the porphyrin ring by metal-ligandcoordinate bond compared with phene compound and the electron/energy may transfer more easily.

Conclusion

This paper describes the synthesis of a triphenylamine ligand designed to complex ZnTPP. The pyridyl-triphenyl-amine was designed to provide direct electronic communication between the porphyrin and the triphenylamine through non-covalent association between the *N*-atom on the pyridine and the Zn^{2+}-atom in the porphyrin core. The photoinduced intra-molecular energy/electron-transfer excited state were proven by photophysical, electrochemical. Our results also indicated that the functional materials with two moieties could be obtained by combination of different functional chromophore into one molecule using a covalent bond linkage. This result may open a new route for developing donor-acceptor systems, which is not severely limited by the synthetic route.

REFERENCES

1. J. Deisenhofer and J.R. Norris, The Photosynthetic Reaction Center, Academic Press, San Diego, USA (1993).
2. J. Deisenhofer, O. Epp, K. Miki, R. Huber and H. Michel, *J. Mol. Biol.*, **180**, 385 (1984).
3. R.A. Wheeler, Introduction to the Molecular Bioenergetics of Electron, Proton and Energy Transfer, ACS Symposium Series, Washington, pp. 1-6 (2004).
4. W. Leibl and P. Mathis, Electron Transfer in Photosynthesis, Imperial College Press, London, p. 117 (2004).
5. S. Fukuzumi, T. Honda, K. Ohkubo and T. Kojima, *J. Chem. Soc. Dalton Trans.*, 3880 (2009).
6. M.R. Wasielewski, *Acc. Chem. Res.*, **42**, 1910 (2009).
7. Y. Araki and O. Ito, *J. Photochem. Photobiol. C*, **9**, 93 (2008).
8. C.G. Claessens and T. Torres, *J. Am. Chem. Soc.*, **124**, 14522 (2002).
9. D. Gonzlez-Rodrguez, T. Torres, M.M. Olmstead, J. Rivera, M.A. Herranz, L. Echegoyen, C.A. Castellanos and D.M. Guldi, *J. Am. Chem. Soc.*, **128**, 10680 (2006).
10. W. Lubitz, F. Lendzian and R. Bittl, *Acc. Chem. Res.*, **35**, 313 (2002).
11. M.L. Anson, *Science*, **93**, 186 (1941).
12. M.E. El-Khouly, D.K. Ju, K.Y. Kay, F. D'Souza and S. Fukuzumi, *Chem. Eur. J.*, **16**, 6193 (2010).
13. A.D. Adler, F.K. Longo, F. Kampus and J. Kim, *J. Inorg. Nucl. Chem.*, **32**, 2443 (1970).
14. M.J. Plater and T. Jackson, *Tetrahedron*, **59**, 4673 (2003).
15. P.C. Dave and D. Srinivas, *J. Porphyr. Phthalocyan.*, **2**, 243 (1998).
16. P. Bhyrappa, V. Krishnan and M. Nethaji, *J. Chem. Soc. Dalton Trans*., 1901 (1993).
17. S.L. Logunov and M. A. Rodgers, *J. Phys. Chem.*, **96**, 8697 (1992).
18. K.M. Kadish, L.R. Shiue, R.K. Rhodes and L.A. Bottomley, *Inorg. Chem.*, **20**, 1274 (1981).
19. C.W. Huang, K.Y. Chiu and SH.H. Cheng, *J. Chem. Soc. Dalton Trans*., 2417 (2005).
20. H.Q. Chen, C.L. Zhou, L. Wang, J.G. Chen, B. Ling and J. Fu, *Spectrochim. Acta A*, **78**, 371 (2011).
21. I. Okura and H. Hosono, *J. Phys. Chem.*, **96**, 4466 (1992).