

Photoinduced single- and double-electron transfer in a photosynthetic model consisting of one-acceptor with four equally linked donors (D_4-A)

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ABSTRACT

Photoinduced electron transfer (PeT) process in a D_4-A model, in which four *p*-amino-phenoxys (donor D) are covalently linked to a zinc phthalocyanine (acceptor A), was examined by laser flash photolysis and fluorescence technique. Not only does the usual intra-molecular photoinduced single-electron transfer occur from *p*-amino-phenoxy to the excited singlet state of A that forms the long-lived monoanion A^{*-} in the supermolecule with a fast rate of 25 ps, but also features different from PeT in the common $D-A$ model were found. The free energy change, transient absorption spectra and associated decay kinetics strongly suggest that photoinduced intra-molecular double-electron transfer occurs concurrently from multidonors to the second lowest excited singlet state of A to form a double-charge separated state $D_2(D^{*+})_2-A^{2-}$ because of the ability of zinc phthalocyanine to catch up to four electrons in the presence of four strong equal donors.

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1. Introduction

The design and synthesis of electron donor-acceptor ($D-A$) systems to mimic the events of the photosynthetic reaction center have been one of the most important goals in chemistry during the past three decades [1–5]. The default photosynthetic model has been the linearly linked one-donor-one-acceptor series, such as $D-A$, D -bridge- A for dyad, $D-A_1-A_2$ for triad, etc., to achieve a single-charge separated state $D^{*+}-A^{*-}$ via photoinduced electron transfer (PeT). Systems containing porphyrins and/or phthalocyanines, etc. are probably the most popular because of their similarity to chlorophylls in the nature.

The synthesis of such linearly linked $D-A$ models, however, usually requires asymmetric path, such as the prevalent statistical condensation in Scheme 1, which also yields A_4 , D_2-A , D_3-A , D_4-A , and D_4 as byproducts that needs to be separated out [6–8]. The synthesis for the D_4-A , or A_4-D , on the other hand, can be carried out by the typical symmetric procedure (bottom of Scheme 1) without the difficulty [9]. The D_4-A system, therefore, has its advantage of easier preparation over $D-A$ if efficient PeT also occurs in it from the viewpoint of practical application.

Surprisingly, there is no report yet on PeT in the D_4-A system. It is not clear if and how PeT will occur in it, since the four donors

may compete or coordinate to lower or increase the rate of PeT. It is the purpose of this study to examine whether PeT occurs in the D_4-A system by using zinc phthalocyanine (ZnPc) as the electron acceptor and four *p*-amino-phenyls as the electron acceptors. ZnPc and compound **1** are used as model compounds with structures shown in Scheme 2.

2. Experimental

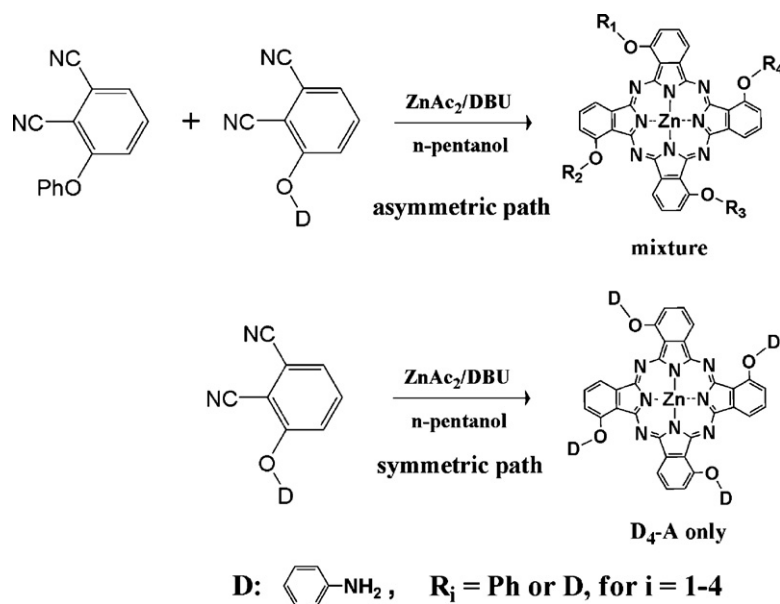
2.1. Synthesis

All organic solvents were dried by appropriate methods and distilled before use, the reagents were of analytical grade and used as received. ZnPc was purchased from Tokyo Kaisei. ¹H NMR spectra were recorded at room temperature on a Bruker dmx 300 MHz NMR spectrometer. MS spectra were recorded on a Bruker APEX II and a Micromass GCT-MS spectrometer. Samples for C, H, N elemental analysis were dried under vacuum, and analyzed with a Carlo Erba-1106 instrument.

2.1.1. 3-Phenoxyphthalonitrile

A mixture of 3-nitrophthalonitrile (6.92 g, 40 mmol), phenol (4.46 g, 48 mmol), and dry potassium carbonate (22.1 g, 160 mmol) was stirred in dry DMF (30 mL) under nitrogen for 24 h at room temperature. The solution was poured into 100 mL ice-water, filtered. The resulting solid was washed with cold deionized water and dried. The crude product was purified by recrystallization with ethanol as solvent (6.90 g, 77% yield). ESI-MS: $m/z = 221.2 [M + 1]^+$.

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Scheme 1. Synthesis of D–A by asymmetric path, and D₄–A by symmetric path.

¹H NMR (CDCl₃): δ, ppm 7.84–7.813 (2H, m, Ar–H), 7.53–7.487 (2H, t, Ar–H, Ar'–H), 7.34–7.21 (4H, m, Ar'–H). IR [(KBr) ν_{max}/cm⁻¹]: 3053 (Ar–H), 2235(CN), 1245 (Ar–O–Ar).

2.1.2. 3-(*p*-Amino-phenoxy)-phthalonitrile

The same procedure for synthesis and purification of 3-phenoxy-phthalonitrile was applied except that *p*-aminophenol (5.23 g, 48 mmol) was employed to replace phenol. Yield: 5.45 g, 57%. ESI-MS: *m/z* = 221.2 [M+1]⁺. ¹H NMR (CDCl₃): δ, ppm 7.84–7.813 (2H, m, Ar–H), 7.53–7.487 (2H, t, Ar–H, Ar'–H), 7.34–7.21 (4H, m, Ar'–H). IR [(KBr) ν_{max}/cm⁻¹]: 3053 (Ar–H), 2235(CN), 1245 (Ar–O–Ar).

2.1.3. 1,8(11),15(18),22(25)-(Tetraphenoxyphthalocyaninato) zinc(II) (**1**)

Zinc acetate (0.023 g, 0.13 mmol), 3-phenoxyphthalonitrile (0.11 g, 0.5 mmol), and 3 ml dried *n*-pentanol were mixed and stirred at 130 °C for 3.5 h under nitrogen atmosphere in the presence of two drops of DBU as catalyst. After cooling down, the solution was dropped into *n*-hexane. The green solid was collected by filtration and washed with *n*-hexane. The crude product was dissolved in CH₂Cl₂ and then filtered. After concentrating, it was passed through a silica gel column, using THF as an eluting solvent. The product was further purified by column chromatography using CHCl₃ as the mobile phase. Yield: 34 mg (29%). UV–vis (DMF): λ_{max} nm (log ε) 380 (4.67), 622 (4.60), 692 (5.26). IR [(KBr) ν_{max}/cm⁻¹]:

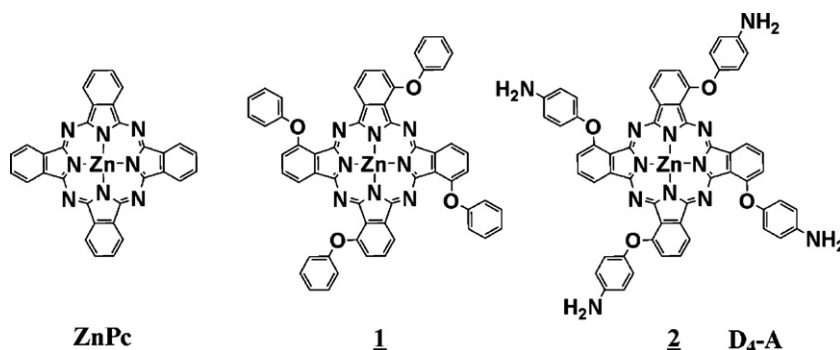
3033 (Ar–CH), 1579 (C=C), 1080 (C–O–C). ¹H NMR (CDCl₃): δ, ppm 8.25–8.93 (4H, m, Pc–H), 7.58–7.97 (4H, m, Pc–H), 7.13–7.52 (24H, m, phenyl–H, Pc–H). Calcd. for C₅₆H₃₂N₈O₄Zn: C 71.08, H 3.41, N 11.84; Found: C 70.80, H 3.75, N 11.48. MALDI-TOF-MS *m/z*: Calculated 944.18; found (M + 1) 944.94.

2.1.4. 1,8(11),15(18),22(25)-(Tetra-*p*-aminophenoxyphthalocyaninato) zinc(II) (**2**)

The procedure for synthesis and purification of **2** was the same as that of **1** except that 3-(*p*-aminophenoxy)phthalonitrile (0.118 g, 0.5 mmol) was employed instead of 3-phenoxyphthalonitrile. Yield: 45 mg (36%). UV–vis (DMF): λ_{max} nm (log ε) 380 (4.85), 626 (4.87), 698 (5.10). IR [(KBr) ν_{max}/cm⁻¹]: 3357, 3423 (N–H), 3033 (Ar–CH), 1598 (C=C), 1495 (C=C), 1247 (Ar–O–Ar). ¹H NMR (CDCl₃): δ, ppm 8.88–8.80 (4H, d, Pc–H), 8.10–8.00 (4H, t, Pc–H), 7.60–7.51 (4H, d, Pc–H), 7.37–7.33 (8H, d, phenyl–H), 6.91–6.85 (8H, d, phenyl–H), 6.82–6.72 (8H, s, N–H). Calcd. for C₅₆H₃₂N₈O₄Zn: C 66.83, H 3.61, N 16.70; found: C 66.350, H 3.95, N 16.48. MALDI-TOF-MS *m/z*: Calcd. 1004.23; found (M + 1) 1005.31.

2.2. Photophysical measurements

DMF and other solvents were dried and freshly distilled before use. Measurements were carried out at room temperature of 22 °C. UV–vis absorption measurements were made with a HP 8451A spectrophotometer in 10 mm quartz cuvettes. Fluorescence spectra



Scheme 2. Chemical Structure of D₄–A, model compound **1**, and ZnPc.

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