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Molecular tweezer based on zinc porphyrin-substituted diarylethene

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Abstract

A molecular tweezer, zinc porphyrin–dithienylethene–zinc porphyrin (ZnP–DTE–ZnP) triad, has been prepared. Triad ZnPor–DTE–ZnPor showed a little electronic communication among the chromophores judged from the comparison of the steady-state absorption and fluorescence spectra for triads and their component compounds. Irradiation of ZnPor–DTE–ZnPor with UV light converts dithienylethene moiety from open form to closed form. The complexation of ZnP–DTE–ZnP with 4,4′-bipyridyl were investigated by absorption and fluorescence spectroscopic measurements. ZnP–DTE–ZnP forms a 1:1 complex with 4,4′-bipyridyl. The stability constants of $\log K = 4.0$ and $4.2\ \mathrm{mol^{-1}\ dm^3}$ were determined by absorption and fluorescence spectral changes, respectively.

Keywords: Zinc porphyrin; Dithienylethene; Molecular tweezer; 4,4′-Bipyridyl; Absorption; Fluorescence

1. Introduction

Porphyrins [1–22] have been received great attention as suitable photoactive components for the study of energy and electron transfer reactions in multicomponent systems and as building blocks for molecular photonic wires, molecular gates, chemosensors, energy conversion systems and other molecular-scale electronic and photonic devices, because of their attractive electronic and redox properties and with the ease of modification by the development of various synthetic routes. Porphyrins have also employed as a typical component in well-defined electron donor–acceptor arrays mimicking the photosynthetic reaction center for the highly efficient photo-induced electron transfer and long-lived charge separation.

Dimeric porphyrins [14–18] have been studied as model systems mimicking natural photosynthetic pigments and various porphyrin dimers have been prepared for investigation of structure–property relationship. Introduction of suitable linker between two porphyrins could give an optimal interporphyrin distance or angle for the electronic communication [12].

One approach may be to employ a photochromic molecule, which undergoes reversible light-induced reaction as a switching component. It is very interesting to devise molecular photonic system with on-off controllable trigger. With photoresponsive linker, the interporphyrin distance or angle can be controlled by light, where photochromic moiety could be isomerized between two isomers with different properties, a short-wavelength absorbing colorless form and a long-wavelength absorbing colored form.

Dithienylethenes (DTE) [23–29] are useful and well-studied photochromic molecules that have been used in various molecular switching applications. DTE undergoes thermally irreversible and photochemically reversible photochromic reactions and shows fatigue resistance. Reversible photochemical isomerization of DTE occurs with excitations at two different wavelengths. The open-form isomer of DTE is cyclized to form the closed-form isomer when irradiated with short wavelength UV light. The closed-form isomer is thermally stable. Upon irradiation with long wavelength visible light, the closed-form isomer converts back to the open-form isomer.

From the viewpoint that the inter-porphyrin distance in bis-porphyrin linked by the photoresponsive chromophore can be controlled by light, we employed dithienylethene as a photoresponsive linker between two zinc porphyrins. While open-form DTE having two zinc porphyrin moieties, ZnP–DTEo–ZnP can bind cooperatively with 4,4′-bipyridyl like a tweezer, closed-form ZnP–DTEc–ZnP cannot bind coorperatively because of its structural rigidity and wider inter-porphyrin distance. Irradiation leads to the geometrical changes of ZnP–DTEc–ZnP and makes the control of affinity to guest molecules possible.

In this study, zinc porphyrin–dithienylethene–zinc porphyrin triad (ZnP–DTE–ZnP) was designed and synthesized.

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The ethylene group is used as a spacer between zinc porphyrin and dithienylethene. The complexation behaviors of ZnP–DTE–ZnP to 4,4′-bipyridyl were examined using absorption and fluorescence spectra.

2. Experimental

2.1. Synthesis

2.1.1. 5-(Methyl-4-benzoate)-10,15,20-tris-(4-methylphenyl)porphyrin (TTP-CO_2CH_3)

5-(Methyl-4-benzoate)-10,15,20-tris(4-methylphenyl)porphyrin (TTP-CO_2CH_3) was prepared according to Lindsey et al. procedure [5] reported for closely related tetraarylporphyrin systems. To 0.49 g (3 mmol) of 4-formylbenzoate and 1.06 mL (9 mmol) of *p*-tolualdehyde in 300 mL of chloroform at room temperature was added 0.83 mL (12 mmol) of pyrrole and 0.4 mL (3.6 mmol) of $BF_3{\cdot}O(Et)_2$. The mixture was stirred for 1 h and then 0.5 g (2.3 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone was added. The reaction mixture was stirred for 1 h and evaporated and dried under vacuum. Column chromatography on silica gel with dichloromethane and hexane gave 0.10 g of TTP-CO_2CH_3 in ca. 4.7% yield. MS: m/e 714 (M^+). ^1H NMR in $CDCl_3$ (400 MHz): δ 8.69–8.81 (8H, m, pyrrole), 8.36 (2H, d, $J = 8.1$ Hz, benzoate), 8.23 (2H, d, $J = 8.1$ Hz, benzoate), 8.02 (6H, d, $J = 7.8$ Hz, tolyl), 7.48 (6H, d, $J = 7.8$ Hz, tolyl), 4.03 (3H, s, ester methyl), 2.63 (9H, s, Ar-CH_3), −2.79 (2H, broad s, pyrrole-NH).

2.1.2. 5-(4-Hydroxymethylphenyl)-10,15,20-tris-(4-methylphenyl)porphyrin (TTP-CH_2OH)

To 15 mg (0.39 mmol) of lithium aluminum hydride dissolved in 13 mL of freshly distilled tetrahydrofuran, 92 mg (0.13 mmol) of TTP-CO_2CH_3 in 13 mL of freshly distilled tetrahydrofuran was added and stirred for 30 min at room temperature. The reaction mixture was poured to 15 mL of 1% HCl and extracted with methylene chloride. The organic layer was dried with Na_2SO_4 and evaporated. Purple solid (78 mg) was obtained in 78% yield. MS: m/e 686 (M^+). ^1H NMR in $CDCl_3$ (400 MHz): δ 8.68–8.80 (8H, m, pyrrole), 8.10 (2H, d, $J = 7.5$ Hz, hydroxymethylphenyl), 8.02 (6H, d, $J = 7.8$ Hz, tolyl), 7.63 (2H, d, $J = 7.5$ Hz, hydroxymethylphenyl), 7.48 (6H, d, $J = 7.8$ Hz, tolyl), 5.22 (2H, s, CH_2OH), 2.63 (9H, s, Ar-CH_3), −2.75 (2H, broad s, pyrrole-NH).

2.1.3. 5-(4-Bromomethylphenyl)-10,15,20-tris-(4-methylphenyl)porphyrin (TTP-CH_2Br)

Thirty-four milligrams (0.05 mmol) of TTP-CH_2OH was dissolved in 15 mL of methylene chloride and stirred in ice bath. Seventy-five microliters of PBr_3 (0.1 M solution in CH_2Cl_2, 0.075 mmol) was added at 0 °C and then warm to room temperature and the solution was stirred for 1 h. The reaction mixture was poured to 50 mL of the cold saturated $NaHCO_3$ aqueous solution and extracted with methylene chloride. The organic layer was dried with Na_2SO_4 and evaporated. Purple solid (17 mg) was obtained in 44% yield. MS: m/e 749 (M^+). ^1H NMR in $CDCl_3$ (400 MHz): δ 8.68–8.80 (8H, m, pyrrole), 8.10 (2H, d, $J = 7.5$ Hz, hydroxymethylphenyl), 8.02 (6H, d, $J = 7.8$ Hz, tolyl), 7.63 (2H, d, $J = 7.5$ Hz, hydroxymethylphenyl), 7.48 (6H, d, $J = 7.8$ Hz, tolyl), 4.78 (2H, s, CH_2Br), 2.63 (9H, s, Ar-CH_3), −2.76 (2H, broad s, pyrrole-NH).

2.1.4. P–DTE–P

Thirty-four milligrams (0.045 mmol) of TTP-CH_2Br was dissolved in 20 mL of toluene and 11.8 mg (0.045 mmol) of triphenylphosphine was added and the solution was refluxed for 2 h under nitrogen flow and then evaporated. Forty-five milligrams (0.045 mmol) of the resulting crude TTP-CH_2PPh_3Br was dissolved in 10 mL of DMSO and 10 mg of $NaOCH_3$ was added and the solution was refluxed for 30 min under nitrogen flow. After adding 12 mg (0.023 mmol) of 1,2-di(2-methyl-4-formyl-3-thiophenyl)perfluorocyclopentene (DTE–CHO) [29], the reaction mixture was refluxed for 5 h. The resulting solution was extracted using CH_2Cl_2 and water. The organic layer was dried with Na_2SO_4 and evaporated. After purification by column chromatography using CH_2Cl_2 as an eluent, 3 mg (yield 12%) of P–DTE–P was obtained. FAB-MS: m/e 1090 (M^+). ^1H NMR in $CDCl_3$ (400 MHz): δ 8.81–8.91 (16H, m, pyrrole), 8.47 (4H, d, $J = 7.5$ Hz, phenyl), 8.34 (4H, d, $J = 7.5$ Hz, phenyl), 8.02 (12H, d, $J = 7.8$ Hz, tolyl), 7.8–7.9 (4H, m, ethylene), 7.63 (2H, s, thiophene), 7.48 (12H, d, $J = 7.8$ Hz, tolyl), 2.73 (18H, s, Ar-CH_3), 2.60 (6H, s, thiophene-CH_3), −2.66 (4H, broad s, pyrrole-NH).

2.1.5. ZnP–DTE–ZnP

P–DTE–P was dissolved in the mixed solvent of CH_2Cl_2/CH_3OH (9/1, v/v) and excess zinc acetate (3 equiv.) was added and stirred for 1 h at room temperature. Zinc insertion was monitored spectroscopically (absorption, fluorescence). The reaction mixture was poured into ethyl acetate, extracted with 5% $NaHCO_3$ and water and then the organic layer was dried with Na_2SO_4 and evaporated. ZnP–DTE–ZnP was obtained following flash chromatography with silica gel. FAB-MS: m/e 1219 (M^+).

2.2. Spectroscopic measurements

^1H NMR spectra were measured on a 400 MHz Bruker Avance 400 NMR spectrometer in chloroform-d_1. EI-Mass and FAB-Mass spectra were measured on Mircomass (UK) Platform GC/LC Mass Spectrometer and JEOL LTD JMS-HX110/110A high resolution tandem mass spectrometer, respectively. Absorption spectra were recorded on a Shimadzu UV-2401PC spectrophotometer. Steady-state fluorescence spectra were recorded on a SLM-Aminco AB2 luminescence spectrophotometer. The concentrations were controlled to be ca. 1×10^{-5} M, where the absorbances of the solutions at the excitation wavelength of 360 nm had usually the value of 0.07–0.08, to avoid inner filter effects. Fluorescence quantum yields Φ_f were determined using 5,10,15,20-tetra(4-methylphenyl)porphyrin (TTP) as a standard ($\Phi_f = 0.09$ in CH_2Cl_2) [30].