

Preparation of a Fluoroionophore Based on Porphyrin-Crown Ether

Eun Ju Shin* and Hyun-Suk Jung

Department of Chemistry, Sunchon National University, Sunchon, Chonnam 540-742, Korea

A porphyrin compound containing a crown ether moiety (Por-Crown) and its zinc complex (ZnPor-Crown) have been prepared and the effect of the addition of alkali metal on their fluorescence has been investigated. As alkali metal cations were added, the absorption and fluorescence maxima did not change. However, the absorbance and intensity of fluorescence increased dramatically. Among the alkali metal cations tested, addition of K^+ and Cs^+ showed strongest enhancement of absorbance and fluorescence intensity of Por-Crown and ZnPor-Crown.

key words: porphyrin, crown ether, fluoroionophore, cation recognition

INTRODUCTION

Sensing and recognition of metal cations using luminescent chemosensors is of current interest. Development of fluoroionophore combining the fluorophore and ionophore is one of the attractive subjects in the studies of chemosensor with selective binding of species and fluorescence as an optimal monitor [1-6]. Ionophore acts as the ion-sensitive receptor and fluorophore as the signal-generator. The sensitivity of fluorophore may be associated with the ionic recognition ability of the ionophore, if the fluorophore may be perturbed by the coordination of cation. According to the nature of the ionophore-fluorophore interaction, the fluorescence signal is modified in intensity or/and in energy [1-7]. Particularly, there is considerable interest for compounds where insertion of a cation into crown ether cavity can change the photophysical properties. Such cation sensing can be observed via the changes in emission intensities, wavelength, and lifetimes by the use of photoinduced electron transfer sensors. Porphyrin is a well-known luminescent and redox active compound that can accomplish the photoinduced electron transfer upon irradiation [8-11]. A crown ether is an ionophore and acts as a substrate binding site that can interact directly with metal cations in solution. Porphyrin attached to crown ether is expected to show the changes of photoluminescence, such as CHEQ (chelation enhanced fluorescence quenching), or CHEF (chelation enhanced fluorescence), depending on binding cations. We have prepared a crown ether appended porphyrin and its cation sensing by fluorescence change has been investigated.

MATERIALS AND METHODS

Synthesis

5-(4-cyanophenyl)-10,15,20-tris(4-methylphenyl)porphyrin (TTP-CN) 5-(4-cyanophenyl)-10,15,20-tris(4-methylphenyl)porphyrin was prepared according to Linsey procedure [12] reported for closely related tetraarylporphyrin systems. To 0.33 g (2.5 mmol) of 4-cyanobenzaldehyde and 0.82 mL (7.5 mmol) of *p*-tolualdehyde in 1 L of chloroform at room temperature was added 0.70 mL (10 mmol) of pyrrole and 0.38 mL (3 mmol) of $BF_3 \cdot O(Et)_2$. The mixture was stirred for 1 hr and then 1.70 g (7.5 mmol) of dichlorodicyanobenzoquinone was added. The reaction mixture was stirred for 1 hr and evaporated and dried under vacuum. Column chromatography on silica gel with dichloromethane and hexane gave 0.10 g of TTP-CN in ca. 6% yield. 1H NMR in $CDCl_3$ (300 MHz): δ 8.70-9.0(8H, m, pyrrole), 8.33(2H, d, $J=8.3$ Hz, 5Ar2-H and 6-H), 8.08(6H, d, $J=8.0$ Hz, 10,15,20Ar2-H and 6-H), 8.04(2H, d, $J=8.3$ Hz, 5Ar3-H and 5-H), 7.55(6H, d, $J=8.0$ Hz, 10,15,20Ar3-H and 5-H), 2.70(9H, s, Ar- CH_3), -2.78(2H, s, pyrrole-NH).

5-(4-carboxyphenyl)-10,15,20-tris(4-methylphenyl)porphyrin (TTP-COOH) 5-(4-carboxyphenyl)-10,15,20-tris(4-methylphenyl)porphyrin was prepared by hydrolysis of 5-(4-cyanophenyl)-10,15,20-tris(4-methylphenyl)porphyrin with strong acid. 5-(4-cyanophenyl)-10,15,20-tris(4-methylphenyl)porphyrin (300 mg, 0.44 mmol) was dissolved in 12 mL of conc. HCl and 20 mL of CF_3COOH . The solution was refluxed under an argon atmosphere for 2 day. The reaction progress was monitored by TLC with 3% methanol/chloroform. $NaHCO_3$ lump was added into the reaction mixture until color changes from green to purple. Purple solid was filtered and rinsed with distilled water and dried. The yield was 87%. The structure was identified by spectral data. Disappearance of IR band at ca. 2230 cm^{-1} indicates absence of CN functional group and C=O and O-H stretch band at ca. 1700 and 3300 cm^{-1} was observed. 1H NMR in $DMSO-d_6$ (300 MHz): δ 8.7-8.9 (8H, m, pyrrole-H), 8.33 (2H, d, $J=8.3$ Hz, 5Ar2-H and 6-H), 8.08 (6H, d, $J=8.0$ Hz, 10,15,20Ar2-H and 6-H), 8.04 (2H, d, $J=8.3$

*To whom correspondence should be addressed.

E-mail : ejs@sunchon.ac.kr

Received August 11, 2004; Accepted August 2, 2004

Hz, 5Ar3-H and 5-H), 7.55 (6H, d, $J=8.0$ Hz, 10,15,20Ar3-H and 5-H), 2.70 (9H, s, Ar-CH₃), -2.63 (2H, s, pyrrole-NH) ppm.

Por-Crown A 100 mg (0.14 mmol) portion of TTP-COOH was dissolved in 40 mL of dry dichloromethane and 28 mg (0.12 mmol) of 1-aza-15-crown-5 and 2.94 mg (0.024 mmol) of dimethylamino-pyridine (DMAP) were added. With stirring the solution under argon, 74 mg (0.36 mmol) of dicyclohexylcarbodiimide (DCC) was added. The solution was refluxed under argon for 1 day. The reaction mixture was evaporated and redissolved with 30 mL of dichloromethane and washed with a saturated aqueous solution of sodium bicarbonate and once with water and dehydrated with sodium sulfate. The solvent was evaporated and the crude product was purified by column chromatography on silica gel with 3% methanol/dichloromethane to afford 41 mg (0.04 mmol, 34% yield) of Por-Crown. ¹H NMR in CDCl₃ (300 MHz): δ 8.74-8.90(8H, m, pyrrole-H), 8.21(2H, d, $J=8.1$ Hz, TTP 5Ar 2-H and 6-H), 8.09(6H, d, $J=7.8$ Hz, 10,15,20Ar 2-H and 6-H), 7.75(2H, d, $J=8.1$ Hz, 5Ar 3-H and 5-H), 7.55(6H, d, $J=7.8$ Hz, 10,15,20 Ar 3-H and 5-H), 3.61-3.68(16H, m, 1-aza-15-crown-5 -CH₂O-), 2.71(9H, s, Ar-CH₃), 2.80-2.83(4H, m, 1-aza-15-crown-5 -CH₂N-), -2.79(2H, s, pyrrole-NH) ppm. FAB-Mass: m/z 987.

ZnPor-Crown A 1:4 methanol:dichloromethane solution of Por-Crown with an excess of zinc acetate was stirred at room temperature for 24 hrs. The solution was chromatographed on a short silica gel column with the same solvent mixture to remove excess zinc acetate and the solvent was evaporated. Dark-purple solid was obtained. The reaction progress was monitored by change of absorption and fluorescence spectra.

Spectroscopic measurements

IR spectra were obtained in KBr pellets on Midac Prospect-IR spectrometer. ¹H NMR spectra were measured on a 300 MHz Bruker DRX300 or 400 MHz Bruker Avance 400 NMR spectrometer in chloroform-*d*₁ or DMSO-*d*₆. EI-Mass and FAB-Mass spectra were measured on Mircomass (UK) Platform II 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 ($\Phi_f=0.12$ in benzene) [13].

RESULTS AND DISCUSSION

The absorption spectra of Por-Crown and ZnPor-Crown in acetonitrile are represented in Figure 1. Their structures are represented in Scheme 1. As shown in Table 1, the absorption spectrum of the reference compounds TTP and TTP-COOH in acetonitrile shows the very intense Soret band with a

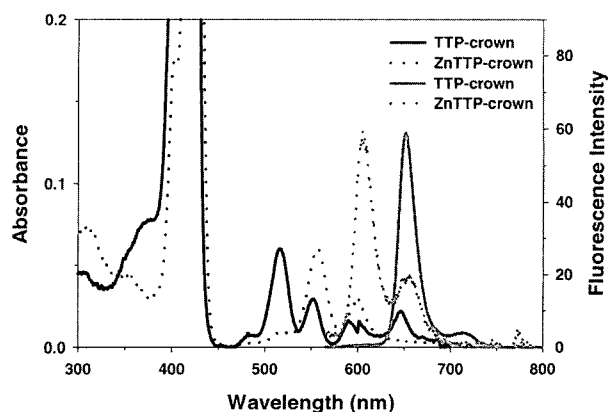
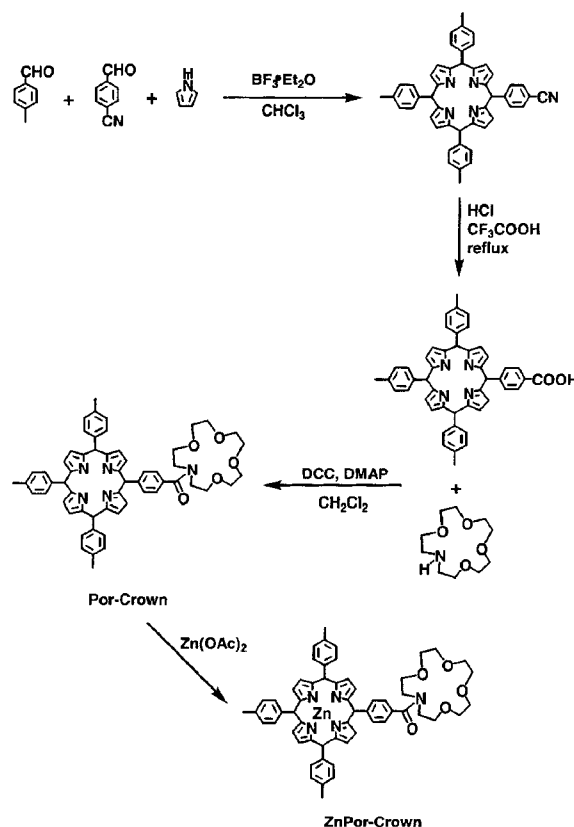


Figure 1. Absorption and fluorescence spectra of Por-Crown and ZnPor-Crown in acetonitrile.



Scheme 1. Synthesis of Por-Crown and ZnPor-Crown.

Table 1. Absorption and fluorescence spectral data of Por-Crown and ZnPor-Crown in acetonitrile.

Compound	λ_{Q1}, nm	λ_f, nm	Φ_f
TTP	646, 591, 549, 513, 415	652, 711	0.09
TTP-acid	646, 591, 549, 513, 415	652, 709	0.08
Por-Crown	646, 591, 549, 513, 415	652, 715	0.08
ZnPor-Crown	597, 556, 422	601, 647	0.05

maximum at 415 nm and the weaker four Q bands at 646, 591, 549 and 513 nm. The absorption spectrum of Por-Crown in acetonitrile is identical to that of TTP and features a Soret

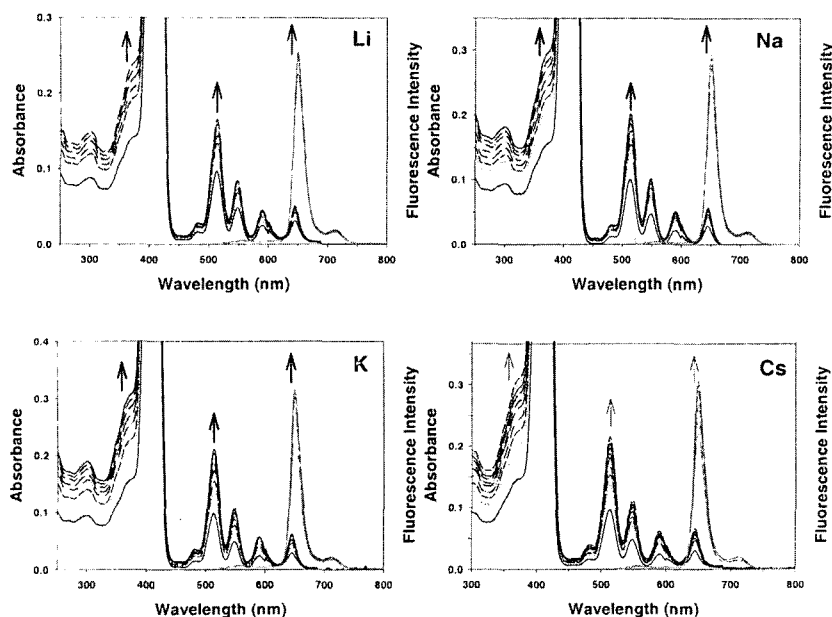


Figure 2. Effect of the addition of alkali metal cation on the absorption and fluorescence spectra of Por-Crown in acetonitrile.

absorption band at 415 nm and four Q bands at 646, 591, 549 and 513 nm, attributable to the TTP moiety. ZnPor-Crown in acetonitrile shows absorption bands at 597, 556 and 422 nm.

Absorption and fluorescence spectral data for Por-Crown, ZnPor-Crown, and the reference compounds TTP and TTP-COOH in acetonitrile at room temperature are collected in Table 1. Fluorescence maxima of Por-Crown appear at 652 and 715 nm, which is slightly red-shifted relative to the reference compound TTP (652 and 711 nm) or TTP-COOH (652 and 709 nm). Fluorescence maxima of ZnPor-Crown appear at 601 and 647 nm. Fluorescence quantum yield for

Por-Crown in acetonitrile ($\Phi_f=0.08$) is similar to that of TTP ($\Phi_f=0.09$). Fluorescence quantum yield for ZnPor-Crown in acetonitrile ($\Phi_f=0.05$) is lower.

Figure 2 shows effect of the addition of alkali metal cation on the absorption and fluorescence spectra of Por-Crown in acetonitrile. Effect of the addition of alkali metal cation on the absorption and fluorescence spectra of ZnPor-Crown in acetonitrile is displayed in Figure 3. No shift of absorption and fluorescence spectra of Por-Crown and ZnPor-Crown was observed on the addition of alkali metal cation as perchlorate salt. However, as alkali metal cations were added, absorbance

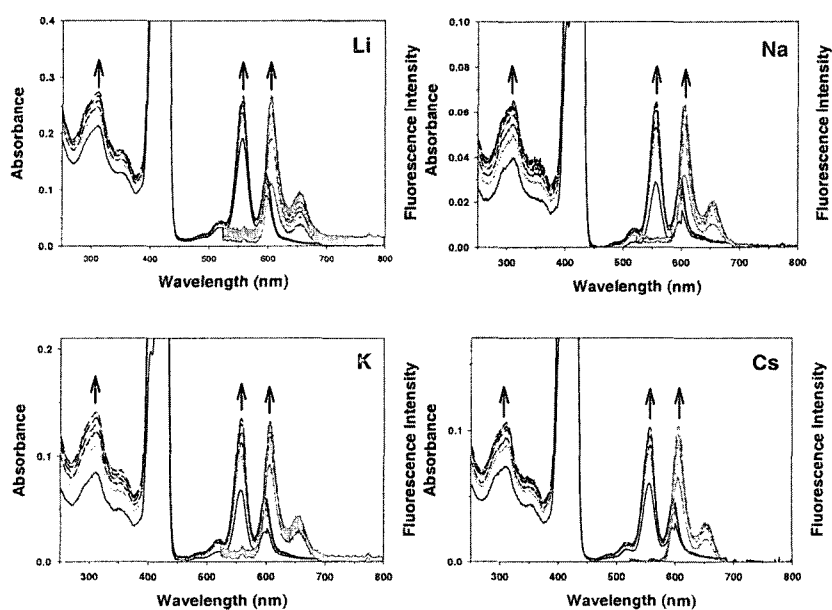


Figure 3. Effect of the addition of alkali metal cation on the absorption and fluorescence spectra of ZnPor-Crown in acetonitrile.

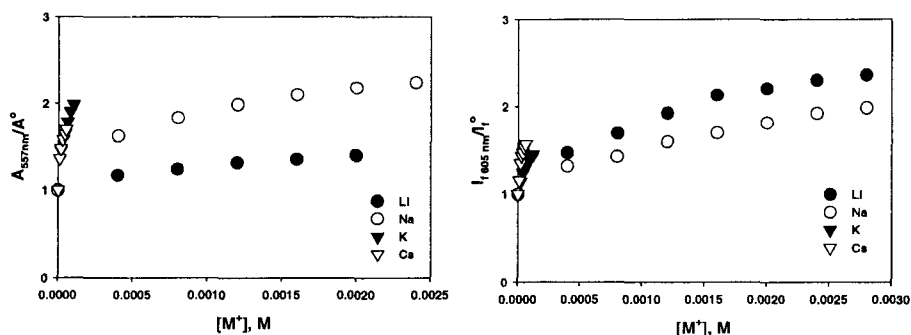


Figure 4. Absorbance (left) and fluorescence intensity (right) changes of Por-Crown with the addition of alkali metal in acetonitrile.

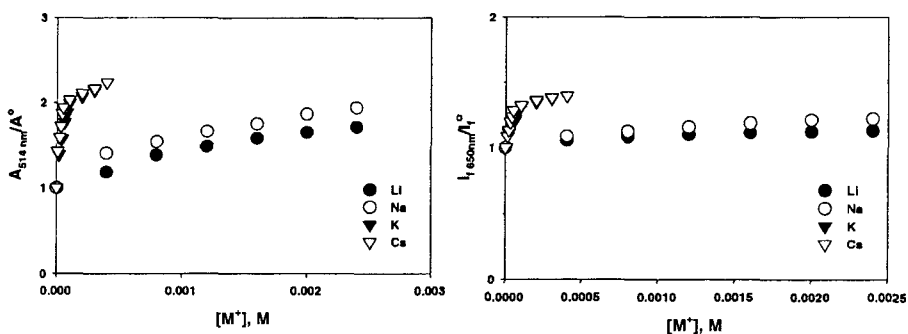


Figure 5. Absorbance (left) and fluorescence intensity (right) changes of ZnPor-Crown with the addition of alkali metal in acetonitrile.

and fluorescence intensity of Por-Crown and ZnPor-Crown were increased. Por-Crown and ZnPor-Crown show CHEF (chelation enhanced fluorescence), depending on binding cations. The photoinduced electron transfer process from electron-rich crown ether moiety to porphyrin is inhibited by complexation of Por-Crown with metal cations, causing the enhancement of fluorescence intensity.

Figure 4 represents the changes of absorbance and fluorescence intensity of Por-Crown with the addition of alkali metal cations such as Li^+ , Na^+ , K^+ and Cs^+ in acetonitrile. Figure 5 shows the changes of absorbance and fluorescence intensity of ZnPor-Crown with the addition of alkali metal in acetonitrile. Absorption and fluorescence spectra of ZnPor-Crown were influenced more strongly than those of Por-crown on the addition of alkali metal cations. Among the alkali metals tested, addition of K^+ and Cs^+ showed strongest enhancement of absorbance and fluorescence intensity of Por-Crown and ZnPor-Crown. Spatial conformation built up between crown ether and peripheral porphyrin moiety as well as size of crown ether cavity might be related to the kind of metal cation exhibiting higher binding affinity. K^+ and Cs^+ are presumably best fitted cations to Por-Crown.

ACKNOWLEDGEMENT

The author would like to thank KBSI for their help in the measurement of NMR and mass spectra. This work was supported by a grant No. 2003-015-C00375 from Korea Research Foundation.

REFERENCES

1. Czarnik, W. (1992) In: *Fluorescent chemosensors for ion and molecule recognition*. American Chemical Society, Washington, D.C.
2. Valeur, B. (1994) In: *Topics in fluorescence spectroscopy. Vol. 4: Probe design and chemical sensing*. Ed. by Lakowicz, J. R. Plenum, New York.
3. Valeur, B. and Leray, I. (2000) Design principles of fluorescent molecular sensors for cation recognition. *Coord. Chem. Rev.* **205**, 3-40.
4. Fabbri, L., Licchelli, M. and Pallavicini, P. (1999) Transition metals as switches. *Acc. Chem. Res.* **32**, 846-853.
5. de Silva, A. P., Gunaratne, H. Q. N., Gunnlaugsson, T., Huxley, A. J. M., McCoy, C. P., Rademacher, J. T. and Rice, T. E. (1997) Signaling recognition events with fluorescent sensors and switches. *Chem. Rev.* **97**, 1515-1566.
6. Czarnik, A. W. (1994) Chemical communication in water using fluorescent chemosensors. *Acc. Chem. Res.* **27**, 302-308.
7. Crochet, P., Malval, J.-P. and Lapouyade, R. (2000) New fluoroionophores from aniline dimer derivatives: a variation of cation signalling mechanism with the number of amino groups. *Chem. Commun.* **2000**, 289-290.
8. Wasielewski, M. R. (1992) Photoinduced electron transfer in supramolecular systems for artificial photosynthesis. *Chem. Rev.* **92**, 435-461.
9. Gust, D., Moore, T. A. and Moore, A. L. (1993) Molecular mimicry of photosynthetic energy and electron transfer. *Acc. Chem. Res.* **26**, 198-205.

10. Balzani, V., Moggi, L. and Scandola, F. (1987) Towards a supramolecular photochemistry: assembly of molecular components to obtain photochemical molecular devices. In: *Supramolecular photochemistry*. Ed. by Balzani, V. D. Reidel, Dordrecht, pp. 1-28.
11. Kalyanasundaram, K. (1992) *Photochemistry of Polypyridine and Porphyrin Complexes*, Academic Press, London, 105 pp.
12. Lindsey, J. S., Prathapan, S., Johnson, T. E. and Wagner, R. W. (1994) Porphyrin building blocks for modular construction of bioorganic model systems. *Tetrahedron* **50**, 8941-8968.
13. Ohno, O., Ogasawara, Y., Asano, M., Kajii, Y., Kaizu, Y., Obi, K. and Kobayashi, H. (1987) Triplet-triplet energy transfer in a copper(II) porphyrin-free-base porphyrin dimer. *J. Phys. Chem.* **91**, 4269-4273.