

A Novel Fluorescent Cesium Ion-Selective Optode Membrane based on 15-Crown-5-Anthracene

Hyo Sook Seo · Sang Hak Lee

Received: 8 August 2010 / Accepted: 25 October 2010 / Published online: 4 November 2010
© Springer Science+Business Media, LLC 2010

Abstract An optode system based on a plasticized polymer membrane containing cesium ion-selective fluoroionophore and lipophilic anions for the determination of cesium ions has been developed. In this work, 15-crown-5 derivative including anthracene was used as a fluoroionophore. Emission intensity of the optode membrane incorporating 15-crown-5-anthracene was measured at 500 nm with excitation at 360 nm in the presence of Tris-HCl buffer solution. Under optimum experimental condition, the relative fluorescence intensity was linear with the concentration of cesium ion in the range of 1.0×10^{-4} M to 1.0×10^{-1} M and the detection limit was obtained 4.2×10^{-5} M, as defined by $LOD = 3 \times S_b/m$ (where S_b =standard deviation of blank signal and, m =slope of the calibration curve). The effect of pH of sample solution on the fluorescent response, the selectivity, response time and reproducibility of the optode membrane were also discussed. The fluorescent optode system shows a high selectivity and sensitivity for cesium ion with respect to other cations such as K^+ , Na^+ and Li^+ .

Keywords Fluorophore · Optode · Cesium · PET

Introduction

There is a growing need to construct chemical sensors for rapid and selective determination of cesium ion in nuclear waste because cesium ion can cause toxicity by replacing

potassium in muscles and red cells. Many methods such as atomic absorption spectroscopy [1–3], radioanalysis [4–6] and ion selective electrodes (ISEs) [7–11] were developed for determination of cesium ion in the past. ISEs were considered as good chemical sensors because they provide high sensitivity and selectivity. However, they are easily affected by electromagnetic interferences, both for the ion-selective electrode and the reference electrode and they also require expensive instrumentation and controlled experimental conditions [12].

One of the methods to remove this limitation is ion-selective optode systems which are advanced techniques in analytical chemistry. They can be miniaturized and manufactured at low cost. Many optode systems for selective recognition of cations were reported in the past decade [12–16]. In these systems, the sensing membrane usually contains a pH sensitive chromophore, a neutral ionophore and a lipophilic anionic site when they are immobilized in polymer matrix. The operation of such an optode usually involves binding of the ion to the ionophore followed by release of a proton from the chromophore, and in the process alters the signal. Despite exhibiting high selectivity, these multi component systems are complex and difficult to optimize. However, once the ionophore and chromophore are linked covalently, the fabrication and optimization of optode systems could be simple. Many studies have been reported. [17–23].

Furthermore, studies on extending the absorption optode systems to fluorescent optode system reveal the possibility to develop highly selective and sensitive optode systems.

In this connection, photo-induced electron transfer (PET) is one of the photophysics mechanisms and used in fluorescent sensors. There are some known fluorescent PET sensors for selective recognition of various ions [24–35]. In these systems signal transduction is derived from the

H. S. Seo · S. H. Lee (✉)
Department of Sensor and Display Engineering and Department
of Chemistry, Kyungpook National University,
Daegu 702-701, Republic of Korea
e-mail: shlee@knu.ac.kr

ability of fluorophore functionalized with a receptor (ionophore) through a spacer to bind an ion, with the fluorescence properties being altered upon binding.

In previous work, the present authors reported a novel fluoroionophore for sensing cesium ion in $\text{CH}_3\text{CN-H}_2\text{O}$ media based on the 15-crown-5-anthracene (Fig. 1) that has crown ether recognition site and the anthracene moiety as fluorescent signal transducer which are connected through an imine linkage; the fluoroionophore exhibited good sensitivity (up to 3.0×10^{-6} M) and selectivity for Cs^+ [36].

In this work, we describe the development of a simple component cesium ion selective optode membrane using 15-crown-5-anthracene. The optode system shows excellent sensitivity and selectivity for Cs^+ with respect to other cations with linear range and detection limit of 1.0×10^{-4} M to 1.0×10^{-1} M and 4.2×10^{-5} M respectively.

Experimental

Apparatus

All the spectrofluorimetric measurements were conducted with a SPEX Fluorolog-2 spectrofluorometer. The spectrometer used a 450-W xenon lamp as the excitation light source and an R 928 photomultiplier tube powered at 950 V as the detector. Fluorescence measurements were carried out in quartz cell of 1-cm path length. Excitation and emission monochromator slit, increment, and integration time were set at 1 mm, 1 nm and 1 s, respectively. A pH meter (Orion, model 95-02) was also used to adjust the pH of solutions and a Kyowariken K-3SPSD-1 Spinner was used to prepare the optode membrane. The thickness of the membrane was measured by a scanning electron microscope (JSM-7401 F, JEOL).

Reagents

All chemicals used were of analytical grade. Potassium tetrakis (4-chlorophenyl) borate (KTPClPB) and metal nitrate salts (LiNO_3 , NaNO_3 , KNO_3 , CsNO_3) were obtained

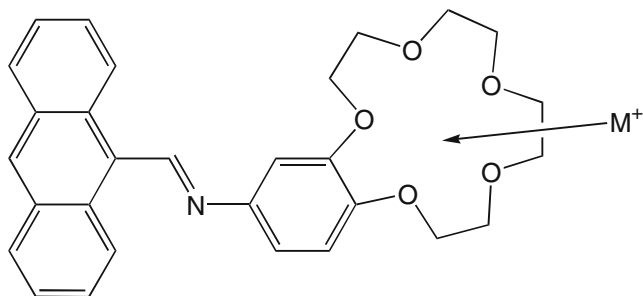


Fig. 1 Schematic representation of interaction between N-(4-benzo-15-crown-5)-anthracene-9-imine and metal ion (M^+)

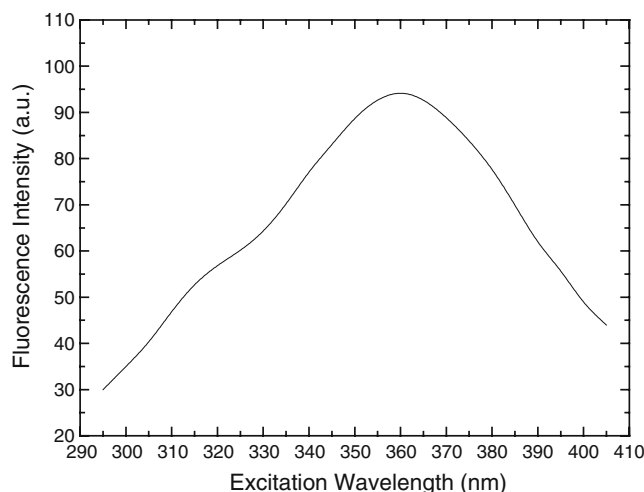


Fig. 2 Excitation spectrum of the optode membrane in Tris-HCl buffer solution (pH=9.0); $\lambda_{\text{em}}=500$ nm

from Aldrich. 15-crown-5-anthracene was kindly gifted by Prof. Jang (Dae-Gu University, Korea).

PVC-PVAc-PVA copolymer, dioctyl phthalate (DOP), tetrahydrofuran (THF) were purchased from Fluka and used for membrane preparation.

A 0.05 M Tris-HCl buffer solution (pH 7.0–9.0) was prepared by dissolving the 25 mmol tris (hydroxyl methyl) aminomethane and 0.1 M HCl in distilled water. The pH was checked by pH meter. Stock solutions of alkali metal ions were prepared by dissolving 99.9% pure metal nitrate salts in Tris-HCl buffer solution. Doubly distilled water was used throughout.

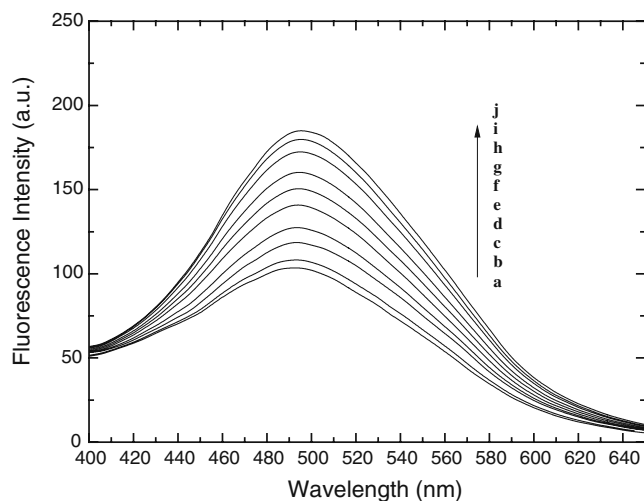


Fig. 3 Fluorescence spectra of the optode membrane in the presence of increasing concentration of Cs^+ ; $\lambda_{\text{ex}}=360$ nm, CsNO_3 concentration of **a** 0 M, **b** 1.0×10^{-5} M, **c** 1.0×10^{-4} M, **d** 3.0×10^{-4} M, **e** 1.0×10^{-3} M, **f** 3.0×10^{-3} M, **g** 1.0×10^{-2} M, **h** 5.0×10^{-2} M, **i** 1.0×10^{-1} M, **j** 1.0 M in Tris-HCl buffer solution (pH=9.0)

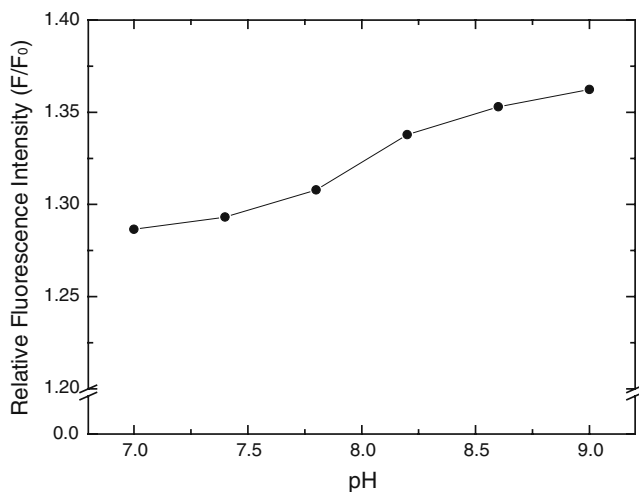


Fig. 4 Effect of pH on the fluorescence enhancement of the optode membrane in a Tris-HCl buffer solution containing 1.0×10^{-3} M CsNO_3 ; $\lambda_{\text{ex}}=360$ nm, $\lambda_{\text{em}}=500$ nm

Membrane preparation

A mixture of 66 mg PVC-PVAc-PVA copolymer, 132 mg DOP, 2 mg potassium tetrakis borate and 3 mg fluoroionophore (15-crown-5-anthracene) was dissolved in 1.0 ml of THF to make a clear and homogeneous solution. An aliquot of 0.25 ml of this solution was applied to the surface of 35 mm × 8 mm thin glass plate which was fixed in a spin-on device (rotating frequency 2500 (5 s): 3500 (25 s): 2500 (5 s) rpm) under a THF-saturated atmosphere. The prepared membrane was coated onto the plate and was dried under ambient conditions for 2 h and stored in the dark. The membrane thickness (4 μm) was experimentally checked using a scanning electron microscope.

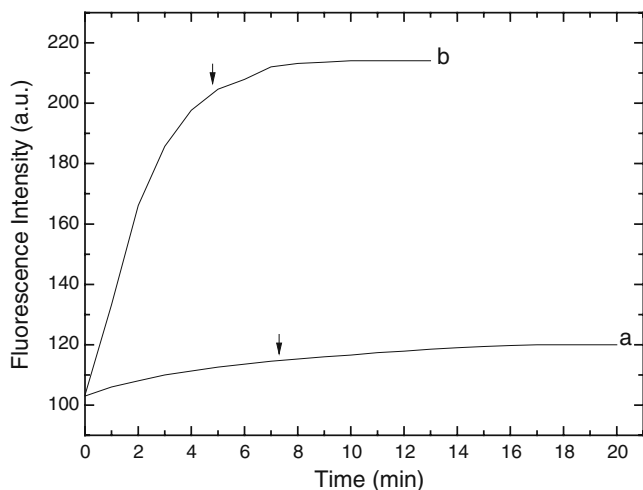


Fig. 5 Response time of the optode membrane, immersed in a Tris-HCl buffer solution containing **a** 1.0×10^{-4} M, **b** 1.0×10^{-1} M CsNO_3

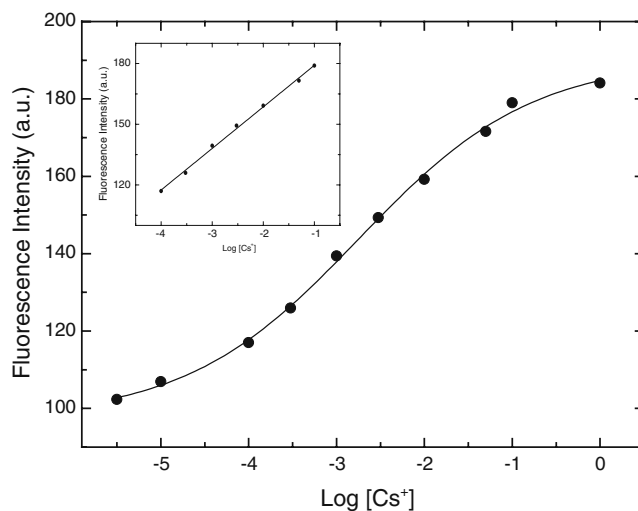


Fig. 6 Response curve of the optode membrane for Cs^+ ; Inset: Linearity of the calibration curve, $\lambda_{\text{ex}}=360$ nm, $\lambda_{\text{em}}=500$ nm

Results and discussion

The excitation spectrum of the optode membrane in Tris-HCl buffer solution (pH=9.0) is shown in Fig. 2. Maximum excitation wavelength was observed at 360 nm and maximum fluorescence intensity was observed at 500 nm with excitation at 360 nm. The fluorescence spectra of the optode membrane in the presence of increasing concentration of Cs^+ ions in Tris-HCl buffer solution (pH=9.0), excited with radiation at a wavelength of 360 nm, are shown in Fig. 3. It showed characteristic emission of anthracene at around 500 nm. As expected, as the concentration of Cs^+ ions increases, the fluorescence intensity of the optode membrane dramatically increases, gaining its maximum value at the concentration of Cs^+ of 1.0 M. As mentioned, 15-crown-5-anthracene (fluoroionophore) has crown ether recognition site (receptor) and the anthracene moiety (fluorophore). In cesium ion free condition, photo-excitation of the fluorophore (15-crown-5-anthracene) produces an electron transfer from the receptor to the fluorophore, resulting in a low fluorescence

Table 1 Ion selectivity coefficients^a of the membrane (at 0.01 M each interfering ion)

System	Interfering ion		
	K^+	Na^+	Li^+
optode 1	-2.1	-2.8	-3.4
optode 2	-2.3	-2.1	-3.2
electrode 1	-2.2	-3.3	-5.1
electrode 2	-2.9	-3.4	-4.4

^a $\text{Log } K_{ij}$: $i=\text{Cs}^+$, $j=\text{interfering ion}$

quantum yield. However, upon cesium bindings, excitation of the fluorophore results in the enhanced fluorescence intensity because cesium ion electrostatically attracts the electron which increases the oxidation potential of the Cs^+ -bound receptor and thermodynamically photo-induced electron transfer (PET) is not favorable, causing the enhanced emission intensity.

Effect of pH of the sample solution on the fluorescent response of the optode membrane has been investigated in Tris-HCl buffer solution containing 1.0×10^{-3} M CsNO_3 . The experiments were carried out in the pH range of 7.0–9.0. As shown in Fig. 4, maximum fluorescence enhancement at 500 nm was obtained in pH 9.0. Fluorescence enhancement of the optode membrane slightly increases along with the increase of pH value. It is assumed that at low pH values, fluorescence enhancement by Cs^+ be decreased due to the increasing protonation of fluoroionophore in the membrane phase. To minimize interference of protonation, the subsequent experiments were performed in pH 9.0 buffer solution.

The response times of optical systems are usually slow compared to the electrochemical systems because a mass transfer of the analyte has to occur before a constant signal is obtained. Thus, reported response times are usually on the order of minutes [13–21]. The response time depends on the membrane thickness (d) and on the diffusion coefficient (D_m) of the species in the membrane phase. $t_{95\%}$ (time needed for 95% of the total signal change to occur) is given approximately by $t_{95\%} = 1.13d^2/D_m$ [12]. If short response times are required, the membranes should be thin. On the other hand, thin membranes lead to a faster leaching of the membrane components and therefore to a reduction of the lifetime. The diffusion coefficient of the membrane depends on the concentration of the membrane components, the PVC contents and the viscosity of the plasticizer. The response time of the prepared membrane ($t_{95\%}$) for 1.0×10^{-4} M and 1.0×10^{-1} M cesium ion was found to be 420 s and 300 s, respectively (Fig. 5). We have used 420 s as a response time of the optode membrane for Cs determination.

The reproducibility of the optical signals was evaluated by changing the concentration of two samples, of cesium ion between 1.0×10^{-3} M and 1.0×10^{-2} M in Tris-HCl buffer solution at pH 9.0. The mean fluorescence values at 500 nm and their standard deviations were obtained from six repeated measurements and were found to be reproducible to $139 \pm 1.90\%$ (1.0×10^{-3} M cesium ion) and $159 \pm 1.63\%$ (1.0×10^{-2} M cesium ion). In defining the short-term stability of the system, the membrane was immersed in a solution of 1.0×10^{-4} M cesium ion at pH 9.0 for 6 h and the fluorescence at 500 nm was determined at hourly intervals. The short-term stability was found to be $117 \pm 2.1\%$ in average of seven measurements.

A linear response of the fluorescence intensity as a function of cesium concentration was observed from 1.0×10^{-4} to 1.0×10^{-1} M as it can be seen Fig. 6. The detection limit calculated as three times the standard deviation of the blank signal was found to be 4.2×10^{-5} M with correlation coefficient of 0.9969.

The optical selectivity of the optode system (optode 1) was investigated for other cations such as Na^+ , K^+ , and Li^+ based on the recommended procedure of Bakker et al [37]. Ion selectivity coefficients, K_{ij}^{opt} ($i = \text{Cs}^+$), corresponds to the value in the case where the signal of each interfering ion at 0.1 M is converted to the concentration of Cs^+ on the basis of the response curve for Cs^+ shown in Fig. 5. We compared it to previous results of other cesium ion selective membrane systems (optode 2 [16] and electrode 1 [10], electrode 2 [11]) and the results summarized in Table 1. It can be noted that the present optode 1 has good selectivity for Cs^+ with respect to Na^+ , K^+ and Li^+ ions and its selectivity is comparable with those of other previously reported systems while these systems operate by different mechanisms.

In this work, we have reported on the development of a new and simplified cesium optode membrane based on 15-crown-5-anthracene. The fluorescent optode membrane offers good linear response and reproducibility and it shows excellent sensitivity and comparable selectivity for Cs^+ in comparison with other optode systems. Studies related to the determination of metal ions using the optode membrane containing other potential fluorophores are in progress.

Acknowledgement This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (KRF-2008-313-C00565).

References

- Sanui H, Pace N (1968) Chemical and ionization interferences in the atomic absorption spectrophotometric measurement of sodium, potassium, rubidium, and cesium. *Anal Biochem* 25:330–346
- Bermejo-Barrera P, Beceiro-Gonzalez E, Bermejo-Barrera A, Martinez FB (1989) Determination of cesium in mineral and thermal waters by electrothermal atomic absorption spectrophotometry. *Microchem J* 40:103–108
- Chekalin NV, Marunkov AG, Pavlutskaia VI, Bachin SV (1991) Determination of traces of Cs, Li and Rb in rocks by laser enhanced ionization spectrometry without preconcentration. *Spectrochim Acta B* 46:551–558
- Shamaev VI, Chudinovskich TV (1982) Determination of cesium in seawater by radiochemical methods. *Anal Chim Acta* 139:177–186
- Theimer KH, Krivan V (1990) Determination of uranium, thorium, and 18 other elements in high-purity molybdenum by radiochemical neutron activation analysis. *Anal Chem* 62:2722–2727

6. Renterghem DV, Cornelis R, Vanholder R (1992) Radiochemical determination of twelve trace elements in human blood serum. *Anal Chim Acta* 257:1–5
7. Saleh MB (1998) New cesium ion-selective electrodes based on anilino-(1, 3-dioxo-2-indanylidene) acetonitrile derivatives. *Talanta* 46:885–895
8. Jeon SW, Yeo HK, Lee HK, Ko SW, Nam KC (2004) Novel Cesium-Selective Electrodes Based on Lipophilic 1, 3-Bisbridged Cofacial-calix[6]crowns. *Electroanalysis* 16:472–477
9. Peper S, Gonczy C, Runde W (2005) Cs⁺-selective membrane electrodes based on ethylene glycol-functionalized polymeric microspheres. *Talanta* 67:713–717
10. Oh HJ, Choi EM, Jeong HS, Nam KC, Jeon SW (2000) Poly (vinyl chloride) membrane cesium ion-selective electrodes based on lipophilic calix[6]arene tetraester derivatives. *Talanta* 53:535–542
11. Berezki R, Csokai V, Grün A, Bitter I, Tóth K (2006) Crown bridged thiocalix[4]arenes as cesium-selective ionophores in solvent polymeric membrane electrodes. *Anal Chim Acta* 569:42–49
12. Seiler K (1993) Ion-selective optode membrane. *Fluka Chemie, CH-9470 Buchs*
13. Yang X, Wang K, Xiao D, Guo C, Xu Y (2000) Development of a fluorescent optode membrane for sodium ion based on the calix[4]arene and tetraphenylporphine. *Talanta* 52:1033–1039
14. Ensafi AA, Fouladgar M (2009) A sensitive and selective bulk optode for determination of Hg(II) based on hexathiacyclooctadecane and chromoionophore V. *Sens Actuators B* 136:326–331
15. Kurihara K, Ohtsu M, Yoshida T, Abe T, Hisamoto H, Suzuki K (2001) Micrometer-sized lithium ion-selective microoptodes based on a “tailed” neutral ionophore and a fluorescent anionic dye. *Anal Chim Acta* 426:11–18
16. Zeng H, Dureault B (1998) Cesium-selective optode membrane based on the lipophilic calix[4]biscrown in the 1, 3-alternate conformation. *Talanta* 46:1485–1491
17. Murkovic I, Oehme I, Mohr GJ, Ferber T, Wolfbeis OS (1995) Optode Membrane for Continuous Measurement of Silver Ions. *Mikrochim Acta* 121:249–258
18. Shamsipur M, Hosseini M, Alizadeh K, Alizadeh N, Yari A, Caltagirone C, Lippolis V (2005) Novel fluorimetric bulk optode membrane based on a dansylamidopropyl pendant arm derivative of 1-aza-4, 10-dithia-7-oxacyclododecane ([12]aneNS2O) for selective subnanomolar detection of Hg(II) ions. *Anal Chim Acta* 533:17–24
19. Benco JS, Nienaber HA, McGimpsey WG (2002) A sodium ion sensor based on a covalently-linked aminorhodamine B-calix[4]arene chromoionophore. *Sens Actuators B* 85:126–130
20. Ertekin K, Tepe M, Yenigül B, Akkaya EU, Henden E (2002) Fiber optic sodium and potassium sensing by using a newly synthesized squaraine dye in PVC matrix. *Talanta* 58:719–727
21. Shamsipur M, Sadeghi M, Alizadeh K, Sharghi H, Khalifeh R (2008) An efficient and selective fluorescent optode membrane based on 7-[(5-chloro-8-hydroxy-7-quinolinyl)methyl]-5, 6, 7, 8, 9, 10-hexahydro-2 H-1, 13, 4, 7, 10 benzodioxatriazacyclopentadecine-3, 11(4 H, 12 H)-dione as a novel fluoroionophore for determination of cobalt(II) ions. *Anal Chim Acta* 630:57–66
22. Shamsipur M, Poursaberi T, Avanes A, Sharghi H (2006) Copper (II)-selective fluorimetric bulk optode membrane based on a 1-hydroxy-9, 10-anthraquinone derivative having two propenyl arms as a neutral fluorogenic ionophore. *Spectrochim Acta Part A* 63:43–48
23. Shamsipur M, Poursaberi T, Karami AR, Hosseini M, Momeni A, Alizadeh N, Yousefi M, Ganjali MR (2004) Development of a new fluorimetric bulk optode membrane based on 2, 5-thiophenylbis(5-tert-butyl-1, 3-benzoxazole) for nickel(II) ions. *Anal Chim Acta* 501:55–60
24. Ooyama Y, Egawa H, Yoshida K (2009) The design of a novel fluorescent PET sensor for proton and water: A phenylamino-naphtho[1, 2-d]oxazol-2-yl-type fluorophore containing proton donor and acceptor groups. *Dyes and Pigments* 82:58–64
25. Gunnlaugsson T, Bichell B, Nolan C (2004) Fluorescent PET chemosensors for lithium. *Tetrahedron* 60:5799–5806
26. de Silva AP, Sandanayake KRAS (1991) Fluorescent PET (photoinduced electron transfer) sensors for alkali cations: optimization of sensor action by variation of structure and solvent. *Tetrahedron Lett* 32:421–424
27. de Silva AP, Gunaratne HQN, McCoy CP (1993) A molecular photoionic AND gate based on fluorescent signaling. *Nature* 364:42–44
28. de Silva AP, Gunaratne HQN, McCoy CP (1997) Molecular Photoionic AND Logic Gates with Bright Fluorescence and “Off-on” Digital Action. *J Am Chem Soc* 119:7891–7892
29. Magri DC, Coen GD, Boyd RL, de Silva AP (2006) Consolidating molecular AND logic with two chemical inputs. *Anal Chim Acta* 568:156–160
30. Fan J, Peng X, Wu Y, Lu E, Hou J, Zhang H, Zhang R, Fu X (2005) A new PET fluorescent sensor for Zn²⁺. *J Lumin* 114:125–130
31. Wang YW, Shi YT, Peng Y, Zhang AJ, Ma TH, Dou W, Zheng JR (2009) Fluorescent sensors for Ca²⁺ and Pb²⁺ based on binaphthyl derivatives. *Spectrochim Acta Part A* 72:322–326
32. Dang F, Lei K, Liu W (2008) A New Highly Selective Fluorescent Silver Probe. *J Fluoresc* 18:149–153
33. Callan JF, Mulrooney RC, Kamila S, McCaughan B (2008) Anion Sensing with Luminescent Quantum Dots—A Modular Approach Based on the Photoinduced Electron Transfer (PET) Mechanism. *J Fluoresc* 18:527–532
34. Du J, Fan J, Peng X, Li H, Wang J, Sun S (2008) Highly Selective and Anions Controlled Fluorescent Sensor for Hg²⁺ in Aqueous Environment. *J Fluoresc* 18:919–924
35. Sung K, Fu HK, Hong SH (2007) A Fe³⁺/Hg²⁺-selective anthracene-based fluorescent PET sensor with tridentate ionophore of amide/β-amino alcohol. *J Fluoresc* 17:383–389
36. Seo HS, Karim MM, Lee SH (2008) Selective Fluorimetric Recognition of Cesium Ion by 15-Crown-5-Anthracene. *J Fluoresc* 18:853–857
37. Bakker E, Bühlmann P, Pretsch E (1997) Carrier-Based Ion-Selective Electrodes and Bulk Optodes. 1. General Characteristics. *Chem Rev* 97:3083–3132