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Anthracylmethyl Benzoazacrown Ether as Selective Fluorescence Sensors for Zn^{2+}

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Abstract: A new benzoazacrown ether fluorescence sensor was synthesized with 9-anthrylmethyl chloride and benzoaza-15-crown-5 in CH_3CN, which particularly shows a strong affinity for Zn^{2+}. Its fluorescence quantum yield increase more than one order of magnitude and a red shift could be noticed when passing from the apolar to the polar solvent.

Keywords: Anthracylmethyl benzoazacrown ether, fluorescence sensors, Zn^{2+}.

Azacrown ethers for its synthetic feasibility compared with all oxygen analogues[1] have been used as important building blocks for constructing host molecules in surpramolecular chemistry[2]. The azacrown ethers with N-substituents bind with metal cation are better than the parent azacrown ethers[3].

PET (photoinduced electron transfer) fluoroionophores, which give rise to a specific emission spectral change upon complexation with guest cations, have attracted considerable attention as spectrophotometric analytical reagents for the detection of particular guest cations[4].

Crown ether fluoroionophores, due to their high sensitivity on emission spectra and selectivity on different cations, can offer great potential for the qualitative and quantitative analysis of various metal ions in chemistry and biology[5]. However, less attention has been paid to the cation binding properties for fluoroionophores with small cage of benzoazacrown ether. Zn^{2+} is widespread used in biology and there is much interest in its detection[6].

Here we report the synthesis and spectroscopic properties of new fluorescent azacrown ether **1** derived from 9-anthrylmethyl chloride and benzoaza-15-crown-5, which particularly shows a strong affinity to Zn^{2+}.

Compound **1** was synthesized with 9-anthrylmethyl chloride and benzoaza-15-crown-5 in CH_3CN under reflux for 4 h, after moving CH_3CN, the needle crystals were obtained, then purified by column chromatography (silica gel with CH_2Cl_2 as eluant) and characterized by ^1H NMR, ^{13}C NMR and MS[7]. Fluorescent spectroscopic data was

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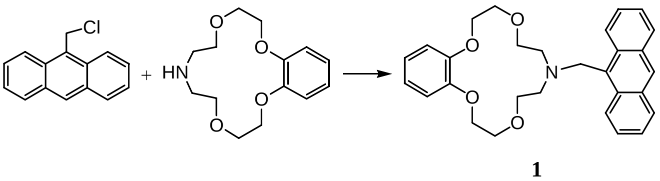
Scheme 1



1

CH_3CN, reflux 4 h, m.p:119.2~120.8 °C (column chromatography, silica gel with CH_2Cl_2), 87.5% yield

Table 1 Fluorescence quantum yield of **1** (10^{-5} mol/L **)** in different solvent*

	Hexane	Dioxane	THF	CH_2Cl_2	CH_3OH	CH_3CN	H_2O
$\lambda_{em\ (nm)}$	418.4	422.4	422.2	422.4	428.4	428.2	430.4
Φ_F	0.0031	0.0087	0.0062	0.0086	0.0629	0.0705	0.1306

*λ_{ex} = 350 nm

determined by using HITACHI F-4500 fluorescence spectrophotometer. **Table 1** gives the fluorescence quantum yield of **1** in different solvents.

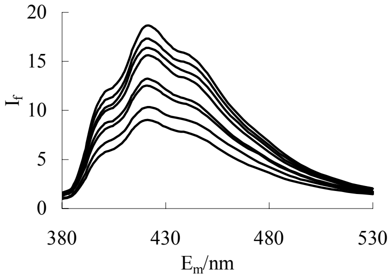
The fluorescence quantum yield and emission wavelength of **1** are strongly sensitive to the solvents, they increase by more than one order of magnitude when passing from the apolar to the polar solvent, the emission wavelength of **1** also shifts to long wavelength from the apolar to the polar solvent.

The fluorescence intensity of **1** in methanol upon alkali and alkaline metals has been illustrated in **Figure 1** using Na^+ as a typical example.

Addition of the sodium salt leads to an increase in the fluorescence intensity of the system, and the fluorescence intensity increase with the increasing of the concentrations of sodium ion.

Table 2 gives the relative fluorescence intensity of **1** with alkali and alkaline metal salts or without metal salts. The addition of Zn^{2+}, Fe^{3+}, Ni^{2+}, Cu^{2+}, Na^+, Mg^{2+}, NH_4^+, K^+, Cs^+, Ca^{2+} ion to methanol solution of **1** leads to the change of fluorescence intensity in the presence of tetramethylammonium hydroxide which eliminated the effect of H^+, the order of change of the fluorescence intensity is $Zn^{2+} > Na^+ > Ni^{2+}$ Y $Mg^{2+} > NH^{4+} > K^+$

Figure 1 Fluorescence emission spectra of **1** (10^{-5} mol/L in methanol, λ_{ex} = 350 nm) with Na^+



(from bottom to top, C_{Na^+} is 0, 10^{-4}, 2.0×10^{-4}, 3×10^{-4}, 5.0×10^{-4}, 7.0×10^{-4}, 9×10^{-4}, 1.1×10^{-3} mol/L)

Table 2 Spectroscopic data of **1** in CH_3OH with different metal ions**

	Na^+	K^+	NH_4^+	Zn^{2+}	Ca^{2+}	Mg^{2+}	Cs^+	Fe^{3+}	Ni^{2+}	Cu^{2+}	Metal-free
λ_{em}(nm)	420.8	419.6	429.0	428.8	419.2	425.2	421.4	--	421.4	421.4	421.8
I/I_0	2.0	1.0	1.5	10.0	1.0	2.0	1.0	0.1	1.5	0.6	1.0

** compound **1** ($C = 10^{-5}$ mol/L) in methanol at 25 ℃ with 10^{-3} mol/L tetramethylammonium hydroxide for eliminated the effect of H^+ and 7×10^{-4} mol/L metal ions [= (M^+)]

Y Cs^+ Y $Ca^{2+} > Cu^{2+} > Fe^{3+}$, and in the presence of K^+, Cs^+, Ca^{2+} the fluorescence spectrum of **1** showed only little change, and the fluorescence intensity of **1** was quenched strongly by addition of Fe^{3+}, Cu^{2+} for energy or electron transfer[8]. Yet the largest effect is observed in case of Zn^{2+} which enhanced the fluorescence intensity about 10 folds.

1 is consists two parts, one is the benzoaza-15-crown-5, the other is anthryl fluorophore, the former is a rigid crown with unsymmetrical shape, which might improve the selectivity to cation, and anthrylmethyl moiety, connecting the nitrogen atom of benzoazacrown *via* methylene group, which also might raise the selectivity to the metal ions. **1** has a more favorable conformation for Zn^{2+} over Na^+, even the size of 15-crown-5 cavity usually matches for Na^+.

Acknowledgments

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References and Notes

1. G. W. Gokel, *Crown Ethers & Cryptands: Monographs in supramolevular Chemistry No.3*; Royal Society of Chemistry: Cambridge, England, **1991**; p79.
2. J. A. Chen, J. L. Lai, G. H. Lee, *Org. Lett.*, **2001**, *3* (25), 3999.
3. (a) N. Mitsunobu, H. Yokono, K. Tomita, *et al.*, *J. Org. Chem.*, **2002**, *67*, 3533; (b) Y. Liu, B. H. Han, Y. Inoue, M. Ouchi, *J. Org. Chem.*, **1998**, *63*, 214; (c) S. Ryoko, M. Takashi, T. Katsumi, *et al.*, *J. Organometallic Chem.*, **2000**, *636* (1-2), 108.
4. (a) A. P. de Silva, H. Q. N. Gunatatne, T.Gunnlauggson, *et al.*, *Chem. Rev.*, **1997**, *97*, 1515; (b) X. Qian, Y. Xiao, *Tetrahedron Lett.*, **2002**, *43*, 2991.
5. (a) E. J. Shin, *Chem. Lett.*, **2002**, 686; (b) A. J. Tong, Y. S. Song, L.-D. Li, *et al.*, *Anal. Chim. Acta*, **2000**, *420*, 57.
6. (a) R. J. P. Willams, *Polyhedron*, **1987**, *6*, 61; (b) B. L. Vallee, D. S. Auld, *Acc. Chem. Res.*, **1993**, *26*, 543; (c) K. M. Hendrickson, J. P. Geue, O. Wyness, *et. al.*, *J. Am.Chem. Soc.*, **2003**, *125*, 3889.
7. **1**: ^{1}HNMR (400MHz, $CDCl_3$) δ(ppm): 2.95 (t, 4H, J=6.0Hz), 3.73(t, 4H, J=6.0Hz), 3.81(t, 4H, J=4.0Hz), 4.11(t, 4H, J=4.0Hz), 4.65(s, 2H), 6.88-6.92(m, 4H), 7.42-7.44(m, 4H), 7.97(d, 2H, J=9.6Hz), 8.39 (s, 1H), 8.55(d, 2H, J=9.2Hz). ^{13}C NMR (400MHz, $CDCl_3$) δ(ppm): 52.65, 54.57, 69.34, 69.68, 70.92, 114.13, 121.37, 124.72, 125.19, 125.46, 127.15, 127.37, 128.80, 130.36, 131.34, 131.40, 133.97, 149.17. ESI MS *m/z*(%): $(M+H)^+$ 458.2(10%), $(M+Na)^+$ 480.2(100%), 481.2(35%)
8. A. W. Varnes, R. B.Dodson, E. L.Wehry, *J. Am. Chem. Soc.*, **1972**, *94*, 946.

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