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# Synthesis and rare earth metal ion-sensing properties of aza-crown derivative incorporating with diaryl-1,3,4-oxadiazole

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## ABSTRACT

A new fluorescent chemosensor (A18C6-Ox) in which a monoaza-18-crown-6 is linked to a diaryl-1,3,4oxadiazole fluorophore by a methylene spacer has been synthesized to evaluate binding interaction with the rare earth ions by means of absorption and emission spectrophotometry. Absorption spectra of A18C6-Ox showed a broad band at 289 nm and there was no significant change in the presence of Sc<sup>3+</sup>, La<sup>3+</sup>, Pr<sup>3+</sup>, Sm<sup>3+</sup>, Cd<sup>3+</sup>, Tb<sup>3+</sup>, Yb<sup>3+</sup> and Lu<sup>3+</sup> except for Ce<sup>3+</sup> and Eu<sup>3+</sup>. From the emission spectral change of A18C6-Ox, interaction of the rare earth ions with A18C6-Ox is very strong. The formation of A18C6-Ox complexing with Sc<sup>3+</sup>, La<sup>3+</sup>, Pr<sup>3+</sup>, Sm<sup>3+</sup>, Gd<sup>3+</sup>, Tb<sup>3+</sup>, Yb<sup>3+</sup> and Lu<sup>3+</sup> leads to an increase in fluorescence intensity of A18C6-Ox, while Ce<sup>3+</sup> and Eu<sup>3+</sup> ions interact strongly causing fluorescence quenching of A18C6-Ox. In addition, the optimal complexation stoichiometry of the rare earth ions with A18C6-Ox was investigated by the fluorescent titration.

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# 1. Introduction

The design and synthesis of functional luminescent probes for metal cations are of growing interest because of their potential applications in biomedical and environmental chemosensors [1] or molecular logic devices [2]. Chemosensors which applied the principle of photoinduced electron transfer are called PET chemosensors. Fluorescent aromatic/heteroaromatic derivatives such as anthracene, pyrene, coumarin and benzothiazole have been widely employed for the construction of PET based chemosensors [3–10]. The sensing abilities of the molecular probes to metal cations strongly relied on the photophysical and electrochemical properties of the fluorophores. Therefore, research for new fluorophores is closely related to further development of PET chemosensors.

Aza-crown ethers can bind with various metal cations because of the nitrogen atoms in the ring, such as alkali metal ions, alkalineearth metal ions, transition metal ions, rare-earth metal ions and so on [11–13]. Diaryl-1,3,4-oxadiazole derivatives are well known to exhibit strong fluorescence and often used as electron-transport materials in electroluminescence devices [14–19], and their applications as the signaling component in molecular sensory systems have been investigated for metal cation recognitions [20–23]. As the chromophoric oxadiazole is an effective electron acceptor, it was expected that the oxadiazole moiety could be used to construct new PET chemosensors. In addition, the radius of RE (III) ion (1.1-1.2 Å) is comparable with the radius of cavity size (1.3 Å) of 18-crown-6 (18-C-6), the complex of RE (III) ion with 18-C-6 by 1:1 molar ration was easily formed, i.e. RE (III) entered in the cavity of the crown ether. In this paper we report the synthesis and fluorescence property of monoaza-18-crown-6 derivative (A18C6-Ox) comprising a diaryl-1,3,4-oxadiazole substituent linked directly to macrocyclic nitrogen atom via a methylene spacer, and investigated the spectral properties of diaryl-1,3,4-oxadiazole chromophore in the presence of RE (III) ions by means of UV–Vis absorption and emission spectrophotometry. The results of our studies concerning the interaction of RE (III) ions (Sc<sup>3+</sup>, La<sup>3+</sup>, Ce<sup>3+</sup>, Pr<sup>3+</sup>, Sm<sup>3+</sup>, Eu<sup>3+</sup>, Gd<sup>3+</sup>, Tb<sup>3+</sup>, Yb<sup>3+</sup> and Lu<sup>3+</sup>) with fluoroionophore are reported.

## 2. Experimental

#### 2.1. Materials and methods

Rare earth oxides were purchased from the Shanghai Yaolong Chemical Factory. Rare earth chlorides were prepared by the method described in the literature [24]. Monoaza-18-crown-6 was purchased from ABCR GmbH & Co. KG. 4-*tert*-Butylbenzoyl chloride was obtained from Alfa Aesar. *P*-Toluic acid and Nbromosuccinimide (NBS) were obtained from Shanghai Zhongqin chemical reagent Co. Ltd. and Tianjin Guangfu Fine Chemical Research Institute, respectively. All of the solvents used were analytical grade reagents.

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Scheme 1. Synthetic routes to A18C6-Ox.

IR spectra (400–4000 cm<sup>-1</sup>) were measured on a Shimadzu IRPrestige-21 FT-IR spectrophotometer. <sup>1</sup>H NMR spectra were obtained on Unity Varian-500 MHz. C, H, and N analyses were obtained using an Elemental Vario-EL automatic elemental analysis instrument. UV–Vis absorption and photoluminescent spectra were recorded on a Shimadzu UV-2550 spectrometer and Perkin Elmer LS-55 spectrometer, respectively. Melting points were measured by using an X-4 microscopic melting point apparatus made in Beijing Taike Instrument Limited Company, and the thermometer was uncorrected.

#### 2.2. Synthesis and characterization of A18C6-Ox

The synthetic routes of A18C6-Ox are described in Scheme 1. *p-Toluic hydrazide: P-*Toluic acid (10 g, 73.5 mmol) was dissolved

in anhydrous ethanol (200 mL), and  $H_2SO_4$  (5 mL) was added dropwise to the stirred solution and the mixture was refluxed for 20 h. The excess ethanol was removed by distillation. The crude product was then stirred vigorously at 80 °C in excessive hydrazine hydrate (20 mL) for 15 h, and the reaction was standed at room temperature overnight. The white precipitate was obtained by filtration, washed with water and ethanol. The product was dried under reduced pressure, and purified with recrystallization from methanol. Yield: 84%. m.p. 115–117 °C. IR (KBr pellet, cm<sup>-1</sup>): 3306, 3225, 3022, 1621, 1351, 830, 722.

1-(4'-Methylbenzoyl)-2-(4'-tert-butylbenzoyl)-hydrazine: 4-tertbutylbenzoyl chloride (17.3 g, 88.3 mmol) was added dropwise to a solution of *p*-toluic hydrazide (13.2 g, 88.3 mmol) in 100 mL of dry pyridine at 0 °C under vigorous stirring. The mixture was heated to reflux for 5 h. After cooled, the mixture was poured carefully into 200 mL of ice water. The white precipitate was collected by filtration, washed with water and dried under vacuum. The crude product was purified by recrystallization from methanol to afford a white solid. Yield: 78%. m.p. 237–238 °C. IR (KBr pellet, cm<sup>-1</sup>): 3225, 2968, 1669, 1635, 1540, 1506, 1277, 1107, 850, 749.

2-(4-methylphenyl)-5-(4-tert-Butylphenyl)-1,3,4-oxadiazole: (12.4 g, 33.9 mmol) of 1-(4'-Methylbenzoyl)-2-(4'-tertbutylbenzoyl)-hydrazine was dispersed in 80 mL of POCl<sub>3</sub> at room temperature. The mixture was refluxed for 10h at 80°C. After cooling, the reaction mixture was poured carefully into 500 mL of ice water under stirring. The precipitate was collected by filtration, washed with water and dried under vacuum. The crude product was purified by recrystallization from methanol to give a white solid. Yield: 81%. m.p. 110-111 °C. IR (KBr pellet, cm<sup>-1</sup>): 2951, 2864, 1615, 1551, 1494, 1416, 1273, 1181, 1118, 1069, 1015, 844, 822 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.0 (d, J = 6.7 Hz, 2H, –ArH), 7.85 (d, J=7.1 Hz, 2H, -ArH), 7.3 (d, J=6.7 Hz, 2H, -ArH), 7.15 (d, J=7.1, 2H, -ArH), 2.3 (s, 3H, -CH<sub>3</sub>), 1.3 (s, 9H, -(CH<sub>3</sub>)<sub>3</sub>).

2-[4-(bromomethyl)phenyl]-5-(4-tert-butylphenyl)-1,3,4-oxadiazole: (5.0g, 17.0 mmol) of 2-(4-methylphenyl)-5-(4-tert-Butylphenyl)-1,3,4-oxadiazole, (3.6 g, 1.2 equiv) of N-bromosuccinimide (NBS) and a catalytic amount of benzoyl peroxide (BPO) were dissolved in 100 mL of carbon tetrachloride. The reaction mixture was refluxed for about 8 h. The warm reaction mixture was filtered under suction and the precipitated succinimide washed with hot CCl<sub>4</sub>. After the solvent was evaporated, the crude product was purified by recrystallization from methanol to afford a white solid. Yield: 85%. m.p. 150–152 °C (lit. m.p. 150–154 °C [21]). IR (KBr pellet, cm<sup>-1</sup>): 3090, 3051, 3011, 2965, 2867, 1615, 1552, 1499, 1422, 1230, 1197, 1100, 1072, 1015, 965, 850, 711.

*N*-[2-(4-methylphenyl)-5-(4-tert-butylphenyl)-1,3,4oxadiazole]aza-18-crown-6 (A18C6-Ox): Under the protection of argon, a mixture of 2-[4-(bromomethyl)phenyl]-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (0.85 g, 2.28 mmol), 1-aza-18-crown-6 (0.50 g, 1.90 mmol) and anhydr. K<sub>2</sub>CO<sub>3</sub> (0.60 g, 4.35 mmol) were dissolved in 30 mL of dry acetonitrile. The reaction mixture was stirred and refluxed for about 5 h. Then the mixture was filtered and the filtrate was concentrated in vacuum. The brown oily mass obtained was extracted with dichloromethane (3 × 50 mL). The combined organic layers were washed with water



Fig. 1. UV–Vis absorption and fluorescence spectra of A18C6–Ox in MeCN solution at room temperature (C = 1.0 × 10<sup>-5</sup> mol/L).

 $(2 \times 50 \text{ mL})$ , and dried over anhydrous MgSO<sub>4</sub>. The solvent was removed in vacuum, and the residue was purified by silica-gel column chromatography using CHCl<sub>3</sub>/CH<sub>3</sub>OH (99:1, v/v) as the eluent to afford pale yellow oil. Yield: 56% (0.58 g). IR (KBr pellet, cm<sup>-1</sup>): 2967, 2874, 1616, 1490, 1343, 1263, 1110, 957, 837, 717. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 8.08 (d, 2H, *J*=6.8 Hz, -Ar-H), 8.06 (d, 2H, *J*=6.6 Hz, -Ar-H), 7.56 (d, 2H, *J*=6.6 Hz, -Ar-H), 7.54 (d, 2H, *J*=6.8 Hz, -Ar-H), 3.78 (s, 2H, -CH<sub>2</sub>-), 3.72-3.63 (m, 20H, -OCH<sub>2</sub>CH<sub>2</sub>-), 2.83 (t, 4H, *J*=7.4 Hz, >NCH<sub>2</sub>CH<sub>2</sub>-), 1.38 (s, 9H, -CH<sub>3</sub>).

#### 3. Result and discussion

#### 3.1. UV absorption spectra

UV absorption spectrum of A18C6-Ox measured in diluted MeCN is shown in Fig. 1. From Fig. 1, A18C6-Ox exhibited a broad absorption band at 289 nm which is similar to MOX because of the same fluorophore diaryl-1,3,4-oxadiazole in the structures of them [21]. The effects of the addition of the selected rare earth ions (Sc<sup>3+</sup>, La<sup>3+</sup>, Pr<sup>3+</sup>, Sm<sup>3+</sup>, Gd<sup>3+</sup>, Tb<sup>3+</sup>, Yb<sup>3+</sup> and Lu<sup>3+</sup>) chlorides on the UV absorption spectra of A18C6-Ox in MeCN solution are shown in Fig. 2.

Addition of MeCN solution of Sc<sup>3+</sup>, La<sup>3+</sup>, Pr<sup>3+</sup>, Sm<sup>3+</sup>, Gd<sup>3+</sup>, Tb<sup>3+</sup>, Yb<sup>3+</sup>, Lu<sup>3+</sup> ( $1.0 \times 10^{-3}$  mol/L) to the MeCN solution of A18C6-Ox ( $1.0 \times 10^{-5}$  mol/L) did not result in any obvious changes either in the shape or the position of absorption spectra of A18C6-Ox, but



**Fig. 2.** Absorption spectra of A18C6-Ox  $(1.0 \times 10^{-5} \text{ mol/L})$  in MeCN and A18C6-Ox containing Sc<sup>3+</sup>, La<sup>3+</sup>, Pr<sup>3+</sup>, Sm<sup>3+</sup>, Gd<sup>3+</sup>, Tb<sup>3+</sup>, Yb<sup>3+</sup> and Lu<sup>3+</sup> (C<sub>M</sub><sup>3+</sup> = 1.0 × 10<sup>-3</sup> mol/L).



**Fig. 3.** Absorption spectra of free  $Ce^{3+}$  ( $1.0 \times 10^{-3}$  mol/L) A18C6-Ox ( $1.0 \times 10^{-5}$  mol/L) in MeCN and A18C6-Ox containing  $Ce^{3+}$  ( $Cce^{3+}$  =  $1.0 \times 10^{-3}$  mol/L).

only a slight increase or decrease in the band intensity. These results show that no significant ground state perturbation of absorption characteristics of the fluorophore was not produced in the presence of the above ions chlorides because of the absence of direct electronic link between the aza-crown and oxadiazole fluorophore [21]. However, the differences appeared in the addition of Ce<sup>3+</sup> and  $Eu^{3+}$  chlorides to the MeCN solution of A18C6-Ox (Figs. 3 and 4). Compared with the absorption spectra of the free Ce<sup>3+</sup> solution and the free A18C6-Ox solution, the absorption spectra of A18C6-Ox with the addition of  $Ce^{3+}$  showed two bands at 266 nm and 316 nm, respectively, which were similar to that of the free Ce<sup>3+</sup> in MeCN solution, and the absorption peak at 289 nm did not appear (Fig. 3). In other words, upon adding chloride of Ce<sup>3+</sup> to the MeCN solution of A18C6-Ox, the UV spectrum of the mixture mainly exhibited the characteristic absorption band of Ce<sup>3+</sup>, which is much stronger than that of the free Ce<sup>3+</sup> at the same concentration, and the absorption band of A18C6-Ox was covered. From Fig. 4. after adding chloride of Eu<sup>3+</sup>, the absorption spectrum of the A18C6-Ox solution also showed the characteristic absorption band of Eu<sup>3+</sup>, the maximal absorption peak was at 282 nm and was stronger than that of the free Eu<sup>3+</sup> in MeCN solution. Similarly, the absorption band of A18C6-Ox was covered. The absorption of free metal ions Ce<sup>3+</sup> and Eu<sup>3+</sup> were stronger, which is the reason why did the absorption band of A18C6-Ox be covered.



**Fig. 4.** Absorption spectra of free  $Eu^{3+}$  ( $1.0 \times 10^{-3}$  mol/L) A18C6-Ox ( $1.0 \times 10^{-5}$  mol/L) in MeCN and A18C6-Ox containing  $Eu^{3+}$  ( $C_{Eu}^{3+}$  =  $1.0 \times 10^{-3}$  mol/L).



**Fig. 5.** Fluorescence spectra of A18C6-Ox  $(1.0 \times 10^{-5} \text{ mol/L})$  in MeCN before and after the addition of Sc<sup>3+</sup>, La<sup>3+</sup>, Ce<sup>3+</sup>, Pr<sup>3+</sup>, Sm<sup>3+</sup>, Eu<sup>3+</sup>, Gd<sup>3+</sup>, Tb<sup>3+</sup>, Yb<sup>3+</sup> and Lu<sup>3+</sup> (C<sub>M</sub><sup>3+</sup> = 1.0 × 10<sup>-4</sup> mol/L).

#### 3.2. Emission spectra

Excitation of A18C6-Ox at its absorption maximum at 289 nm produced emission band at 358 nm which presumably originates from the locally excited stated (Fig. 1). Addition of the selected rareearth chlorides (Sc<sup>3+</sup>, La<sup>3+</sup>, Ce<sup>3+</sup>, Pr<sup>3+</sup>, Sm<sup>3+</sup>, Eu<sup>3+</sup>, Gd<sup>3+</sup>, Tb<sup>3+</sup>, Yb<sup>3+</sup>, Lu<sup>3+</sup>) upto a concentration of  $1.0 \times 10^{-4}$  mol/L to a MeCN solution of A18C6-Ox ( $1.0 \times 10^{-5}$  mol/L) led to no noticeable shift either in the shape or position of the emission spectra (Fig. 5). However, the luminescence intensities were increased or decreased in various degrees depending upon the nature of the cations.

From Fig. 5, addition of Sc<sup>3+</sup>, La<sup>3+</sup>, Pr<sup>3+</sup>, Sm<sup>3+</sup>, Gd<sup>3+</sup>, Tb<sup>3+</sup>, Yb<sup>3+</sup> and Lu<sup>3+</sup> chlorides produced several folds enhancements of fluorescence, the order of emission enhancement being La<sup>3+</sup> > Gd<sup>3+</sup> > Sc<sup>3+</sup>  $\approx$  Yb<sup>3+</sup> > Pr<sup>3+</sup>  $\approx$  Tb<sup>3+</sup> > Lu<sup>3+</sup>  $\gg$  Sm<sup>3+</sup>. However, with the addition of Eu<sup>3+</sup> and Ce<sup>3+</sup>, the fluorescence intensity of A18C6-Ox was induced quenching, and the highest quenching efficiency is observed for  $Ce^{3+}$ . The results were suggested that the singlet (S<sub>1</sub>) and the triplet  $(T_1)$  of A18C6-Ox are lower than the lowest 4f levels of Sc<sup>3+</sup>, La<sup>3+</sup>, Pr<sup>3+</sup>, Sm<sup>3+</sup>, Gd<sup>3+</sup>, Tb<sup>3+</sup>, Yb<sup>3+</sup> and Lu<sup>3+</sup>, but are higher than the lowest 4f levels of Eu<sup>3+</sup> and Ce<sup>3+</sup>. So diaryl-1,3,4-oxadiazole-to-Eu<sup>3+</sup> or Ce<sup>3+</sup> energy transfer mechanism can be invoked to explain the observed fluorescence quenching by Eu<sup>3+</sup> or Ce<sup>3+</sup>. In the case of Ce<sup>3+</sup> ion, the radiationless energy transfer process from diaryl-1,3,4-oxadiazole (energy donor) to Ce<sup>3+</sup> ion (energy acceptor) is highly probable because of a strong overlap of the emission spectrum of diaryl-1,3,4-oxadiazole and absorption spectrum of Ce<sup>3+</sup> ion (Figs. 1 and 3). In the case of Eu<sup>3+</sup> ion a lower overlap of the emission spectrum of diaryl-1,3,4-oxadiazole and absorption spectrum of Eu<sup>3+</sup> ion causes a lower fluorescence quenching of A18C6-Ox by this ion (Figs. 1 and 4). The special phenomenon observed from Eu<sup>3+</sup> and Ce<sup>3+</sup> indicates that A18C6-Ox has selected effect on Eu<sup>3+</sup> and Ce<sup>3+</sup> at certain extent which can let us distinguish Eu<sup>3+</sup> and Ce<sup>3+</sup> from the other rare earth metal ions.

Figs. 6 and 7 show the plots of changes in fluorescent intensity of A18C6-Ox as a function of increasing  $Tb^{3+}$  and  $Lu^{3+}$  ions concentration in MeCN solvent, respectively. At the beginning, with the increase of the ions concentration, the fluorescent intensity also increased. As expected, addition of ca. I equiv of  $Tb^{3+}$  or  $Lu^{3+}$  to a solution of A18C6-Ox in MeCN led to an approximate plateau indicating 1:1 complexation stoichiometry. The fact indicates that the cavity of the aza-18-crown-6 could accommodate one rare earth metal ion.



Fig. 6. Variation in fluorescence intensity of a solution of A18C6-Ox in MeCN  $(1.0 \times 10^{-5} \text{ mol/L})$  at 358 nm as a function of equivalents of Tb<sup>3+</sup> ions.



**Fig. 7.** Variation in fluorescence intensity of a solution of A18C6-Ox in MeCN  $(1.0 \times 10^{-5} \text{ mol/L})$  at 358 nm as a function of equivalents of Lu<sup>3+</sup> ions.

#### 4. Conclusions

A new PET based fluorescent chemosensor (A18C6-Ox) has been synthesized and its absorption and emission spectra investigated in the presence of the selected rare-earth metal ions. While, the absorption spectra of A18C6-Ox had no obvious shifts when exposed to the various selected metal ions except for Ce<sup>3+</sup> and Eu<sup>3+</sup>, significant emission enhancements of A18C6-Ox were detected in the presence of Sc<sup>3+</sup>, La<sup>3+</sup>, Pr<sup>3+</sup>, Sm<sup>3+</sup>, Gd<sup>3+</sup>, Tb<sup>3+</sup>, Yb<sup>3+</sup> and Lu<sup>3+</sup> chlorides, the highest emission enhancements were caused by La<sup>3+</sup> and Gd<sup>3+</sup> ions. The quenching of fluorescence of A18C6-Ox was observed in the presence of Ce<sup>3+</sup> and Eu<sup>3+</sup> chlorides. The result showed that the 1:1 complexes between A18C6-Ox and the selected rare-earth metal ions were formed in MeCN solutions.

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