

# Metal Ion Enhanced Phosphorescence of 2,3-Naphtho-10-aza-15-crown-5: A Possible Molecular Photonic Operator

LI, Li-Qian<sup>a</sup>(李力前)    ZHANG, Li-Ping<sup>\*a</sup>(张丽萍)    WU, Li-Zhu<sup>a</sup>(吴骊珠)  
WANG, Bo-Jie<sup>a</sup>(王波杰)    TUNG, Chen-Ho<sup>a</sup>(佟振合)    CHE, Chi-Ming<sup>b</sup>(支志明)

<sup>a</sup>Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100101, China

<sup>b</sup>Department of Chemistry, The University of Hong Kong, Hong Kong, China

A novel crown ether, 2,3-naphtho-10-aza-15-crown-5 (NAC) was synthesized. This compound does not show strong fluorescence and phosphorescence due to photoinduced intramolecular electron transfer from the nitrogen lone pair of electrons to the singlet excited state of the naphthalene chromophore. Complexation with heavy-metal ions results in the quenching of the fluorescence and enhancement of the phosphorescence significantly. These observations were interpreted in terms of the binding interactions, between the nitrogen lone pair electrons and the metal cation, which prevent photoinduced intramolecular electron transfer, and the heavy-atom effects which induce quenching of the fluorescence and enhancement of the phosphorescence. These azacrown and heavy-metal-based systems could be useful as potential chemical sensors and molecular photonic devices.

**Keywords** photoinduced intramolecular electron transfer, energy transfer, 2,3-naphtho-10-aza-15-crown-5

## Introduction

Molecular systems that combine binding ability and photochemical/photophysical properties are of great interest as sensors in biomedical research<sup>1,2</sup> and as chemical logics<sup>3,4</sup> in molecular information processing. A photonic molecular device/sensor is defined as an assembly of molecular components which, because of the specific arrangement of the components in the dimensions of space and energy, are able to perform light-induced functions. A number of macrocyclic hosts with nitrogen

donors and covalently linked aromatic fluorophores have been studied as chemical sensors and molecular devices.<sup>5-10</sup> In such systems, the binding of a metal ion to a host molecule (signal input) results in an enhancement in fluorescence intensity (signal output), since the lone pairs of the electrons on the nitrogen are engaged in the binding, thus preventing the photoinduced electron transfer from nitrogen to the aromatic fluorophore and allowing the fluorescence to occur. Most systems use alkali/alkaline earth metal ions as inputs. With few exception,<sup>4,5</sup> transition metal ions, particularly heavy atom ions in general can not function as efficient signal inputs, because they quench the fluorescence of aromatic fluorophore very effectively. However, such heavy metal ion-based systems are of particular interests in biomedical sensors.

Although molecular photonic devices/sensors based on fluorescent signaling systems with metal ions have been extensively investigated, it is curious that use of chelation-enhanced phosphorescence to make chemosensors and photonic molecular devices are rarely reported. It has been well established that crown ether hosts with nitrogen donors and covalently linked aromatic chromophores can form complexes with heavy atom ions.<sup>11,12</sup> Such complexation would prevent the photoinduced electron transfer from the nitrogen to the singlet excited state of the chromophores, thus would enhance the phosphorescence quantum yield, because the singlet state

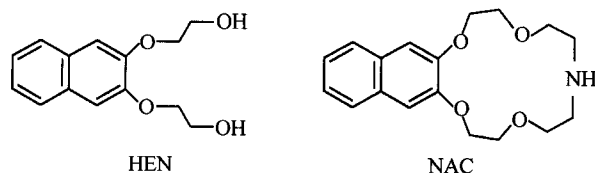
\* E-mail: kjc@ipc.ac.cn

Received May 14, 2001; revised July 18, 2001; accepted September 3, 2001.

Project supported by the Ministry of Science and Technology of China (Nos. G 2000078104 and G 2000077502) and the National Natural Science Foundation of China (Nos. 20073051 and 29972042).

quenching due to photoinduced intramolecular electron transfer would no longer compete with the intersystem crossing from the singlet to triplet excited states. Furthermore, this intersystem crossing process would also be enhanced upon complexation by the heavy-metal effect.<sup>13-16</sup> Thus, it might be expected that combination of the bonding effects with the heavy-atom effects would make sensors/devices based on phosphorescent signaling systems very efficient. In the present work, the case for 2,3-naphtho-10-aza-15-crown-5 (NAC) (Scheme 1) as the hosts is reported. Through the examination of the fluorescence and phosphorescence of the above crown ether in the presence of heavy-metal ions, we demonstrated that these systems might function as chemical sensors and molecular devices.

**Scheme 1** Structure of NAC and HEN



## Results and discussion

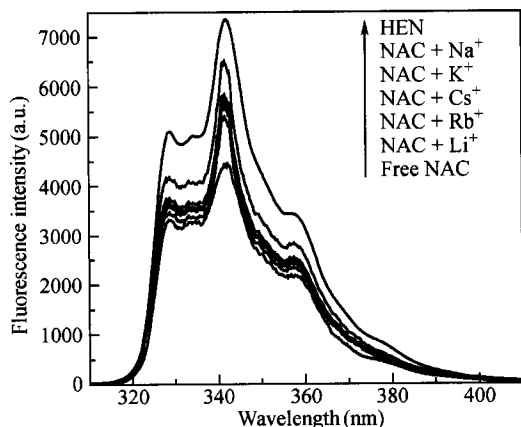
### *Fluorescence and phosphorescence spectra of NAC in the presence of alkali-metal ions*

To obtain the evidence for the complexation of the azacrown ether with metal cations, the fluorescence spectra of NAC in the presence of alkali-metal ions were examined. Fig. 1 shows the fluorescence spectra of NAC in ethanol. In the absence of metal ions NAC exhibited a well-resolved naphthalene monomer emission with maxima at 327, 341 and 358 nm, and no emission from excimer and intramolecular exciplex between the nitrogen atom and the naphthalene  $\pi$ -system was detected. The fluorescence intensity was much weaker compared with the model compound 2,3-bis(2-hydroxyethoxy)naphthalene (HEN) under identical conditions, which might be due to the intramolecular electron transfer from the lone pair of electrons of nitrogen to the singlet excited state of the naphthalene. The free energy change ( $\Delta G$ ) involved in a photostimulated primary electron transfer process can be estimated by Rehm-Weller equation.<sup>17-19</sup>

$$\Delta G = E_{\text{ox}}(\text{D}) - E_{\text{red}}(\text{A}) - \Delta E_{00} - e^2/\epsilon a \quad (1)$$

Where  $\Delta E_{00}$  is the excited state energy, and in this case represents the singlet excited state energy of the model compound HEN. This energy was estimated from its fluorescence spectrum to be 375 kJ/mol.  $E_{\text{ox}}(\text{D})$  and  $E_{\text{red}}(\text{A})$  are the redox potential of the donor and acceptor, respectively, and in this case the oxidation potential of diethylamine (a model compound for the donor) is *ca.* 2.19 V vs. SCE,<sup>20</sup> and the reduction potential of HEN was measured to be *ca.* -1.56 V vs. SCE.  $e^2/\epsilon a$  is the Coulombic interaction in the ion pair state whose magnitude depends on the distance ( $a$ ) between the donor and acceptor radical ion pair and on the dielectric constant ( $\epsilon$ ) of the medium separating the charges. For a contact ion pair in polar solution, this term generally shows only a minor impact on  $\Delta G$ .<sup>11, 17-19</sup> Calculation according to Eq. (1) reveals that electron transfer from the nitrogen to the singlet excited state of the naphthalene chromophore is exothermic by *ca.* -13 kJ/mol. Thus, the low fluorescence yield of NAC relative to the model compound is attributed to the electron transfer from the nitrogen to the singlet excited state of the naphthalene chromophore. The fluorescence intensity increases when an alkali-metal cation is used as an input (Fig. 1). The extent of the fluorescence enhancement depends upon the nature of the metal ions. The size of  $\text{Na}^+$  may match well with the cavity of NAC.<sup>21</sup> The bonding interactions between  $\text{Na}^+$  and the lone pair of electrons of nitrogen would be strongest among the alkali-metal ion complexes. Thus,  $\text{Na}^+$  shows the highest fluorescence enhancement among the alkali-metal ion inputs (Fig. 1). The binding abilities of the small size cation  $\text{Li}^+$  and the large size cations  $\text{K}^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$  toward NAC would be smaller compared with those of  $\text{Na}^+$ . Furthermore, in the complexes of  $\text{Rb}^+$  and  $\text{Cs}^+$ , the ions might exhibit heavy-atom effects on the naphthalene chromophore,<sup>13-16</sup> *i. e.* increasing the intersystem crossing efficiency and quenching the fluorescence of the chromophore. Hence, two mechanisms in the effects of  $\text{Rb}^+$  and  $\text{Cs}^+$  on the fluorescence of the chromophore are operative in opposite directions: binding with the lone pair of electrons of nitrogen increases the fluorescence intensity, while heavy-atom effect decreases the fluorescence. The combination of the two effects results in the smaller fluorescence enhancement compared with  $\text{Na}^+$  as the input (Fig. 1). The fluorescence lifetime measurements confirm the above effects. The lifetimes of the NAC fluorescence in the presence of  $\text{Rb}^+$  and  $\text{Cs}^+$  are

comparable with that in the absence of a metal ion (*ca.* 11.5 ns, Table 1), while the fluorescence lifetime in the presence of  $\text{Na}^+$  is much longer (*ca.* 16.0 ns).



**Fig. 1** Fluorescence spectra of NAC and their complexes with alkali-metal ions in ethanol at 300 K;  $[\text{NAC}] = 2 \times 10^{-4}$  mol/L,  $[\text{Metal chloride}] = 1 \times 10^{-3}$  mol/L; excitation wavelength  $\lambda_{\text{ex}} = 280$  nm.

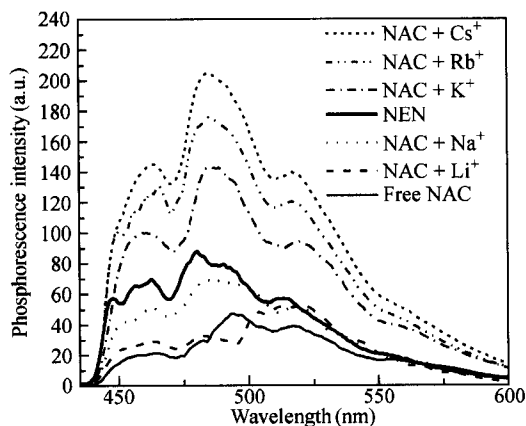
**Table 1** Lifetimes (ns) of NAC in ethanol solution in the presence of alkali-metal cations<sup>a</sup>

Free NAC	$\text{Li}^+$	$\text{Na}^+$	$\text{K}^+$	$\text{Rb}^+$	$\text{Cs}^+$
11.3	12.2	16.1	12.1	11.7	11.8

<sup>a</sup> $[\text{NAC}] = 2 \times 10^{-5}$  mol/L,  $[\text{MCl}] = 1 \times 10^{-3}$  mol/L, excitation wavelength  $\lambda_{\text{ex}} = 280$  nm.

The enhancement of the phosphorescence of NAC is even more significant compared with that for fluorescence when the metal ions are used as the inputs. The phosphorescence spectra of NAC in ethanol glassy matrix at 77 K are shown in Fig. 2. In the absence of a metal ion the phosphorescence of NAC is weaker compared with the model compound HEN, which is evidently due to the photoinduced intramolecular electron transfer in the singlet excited state, which competes with intersystem crossing process and reduces the phosphorescence quantum yield. Complexation of NAC with alkali-metal ions will prevent the photoinduced intramolecular electron transfer to occur. Therefore, the phosphorescence is partially or totally recovered in the presence of a metal ion. Particularly in the case of  $\text{Rb}^+$  and  $\text{Cs}^+$  as the inputs, the heavy-metal effect enhances the intersystem crossing of the naphthalene chromophore from its singlet excited state to the triplet state, thus increasing the phosphorescence yield. The superposition of the bonding effect and

heavy-atom effect allows the phosphorescence to be remarkably enhanced. Table 2 shows the relative phosphorescence quantum yields for NAC in the presence of  $\text{Rb}^+$  and  $\text{Cs}^+$ , which increase by a factor of 3.9 and 4.6, respectively.



**Fig. 2** Phosphorescence spectra of NAC and their complexes with alkali-metal cations in ethanol glass at 77 K;  $[\text{NAC}] = 2 \times 10^{-4}$  mol/L,  $[\text{Metal chloride}] = 1 \times 10^{-3}$  mol/L; excitation wavelength  $\lambda_{\text{ex}} = 320$  nm.

**Table 2** Relative quantum yields of phosphorescence ( $\Phi_p$ ) of NAC in ethanol glass at 77 K in the presence of heavy-metal cations<sup>a</sup>

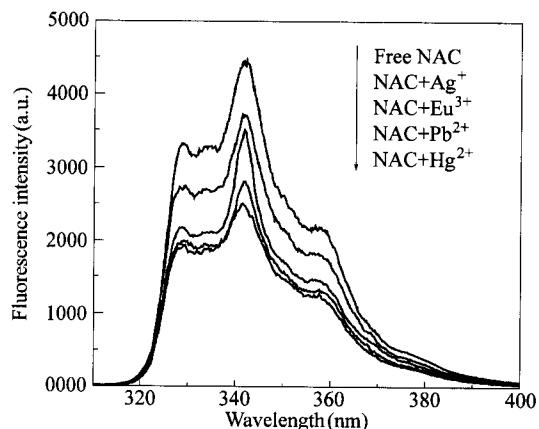
Ion	Free NAC	$\text{Rb}^+$	$\text{Cs}^+$	$\text{Hg}^{2+}$	$\text{Pb}^{2+}$	$\text{Ag}^+$	$\text{Eu}^{3+}$
$\Phi_p$	1.00	3.9	4.6	7.3	5.8	4.4	0.8

<sup>a</sup> $[\text{NAC}] = 2 \times 10^{-4}$  mol/L,  $[\text{Metal ion}] = 1 \times 10^{-3}$  mol/L, excitation wavelength  $\lambda_{\text{ex}} = 280$  nm.

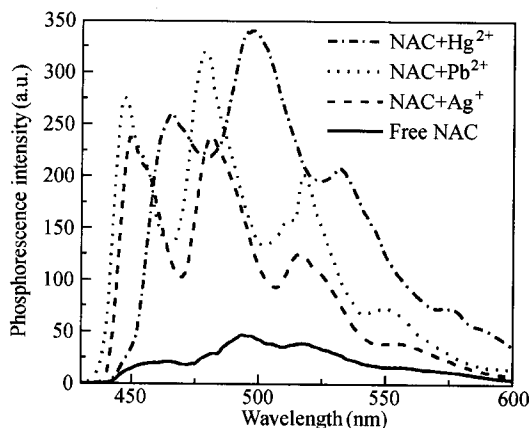
#### Effect of heavy-metal cations

Heavy-metal cations  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Ag}^+$  as inputs for NAC were particularly examined. In contrast to the alkali-metal ions, complexation of NAC with all of the three metal ions induces the decrease in the fluorescence intensity of the naphthalene chromophore in ethanol solution (Fig. 3), suggesting that the heavy-atom effect is more profound in this case compared with the effect of the bonding interactions between the ions and the nitrogen lone pair electrons. On the other hand, the phosphorescence signal undergoes drastic enhancement (Fig. 4) when these ions complex with NAC. Table 2 gives the relative quantum yields of the phosphorescence in the presence of heavy-metal ions. The phosphorescence spectra of the complexes become more struc-

tured relative to that of uncomplexed NAC. This result suggests that heavy-metal ions bound to the crown cavity in NAC impart more rigidity to the molecule than that in the case of the free crown ether. Furthermore, the spectra are remarkably blue-shifted, particularly for the complexes with  $\text{Pb}^{2+}$  and  $\text{Ag}^+$ . Thus, cation binding to the crown leads to an increase in the energy splitting of the triplet-ground states of the naphthalene chromophore. This observation has been well precedented.<sup>14-16</sup>



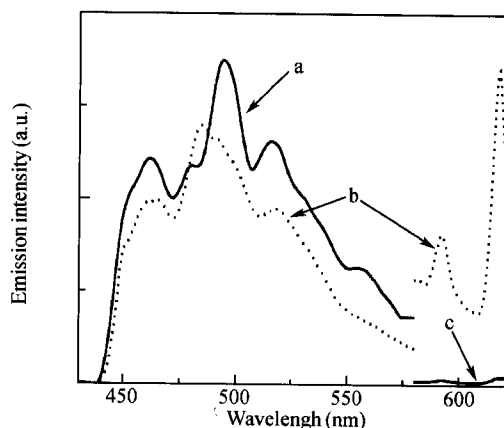
**Fig. 3** Fluorescence spectra of NAC and their complexes with heavy metal ions in ethanol at 300 K;  $[\text{NAC}] = 2 \times 10^{-4}$  mol/L,  $[\text{Metal ion}] = 1 \times 10^{-3}$  mol/L, excitation wavelength  $\lambda_{\text{ex}} = 280$  nm. The counter ions for  $\text{Ag}^+$ ,  $\text{Eu}^{3+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  are  $\text{NO}_3^-$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$  and  $\text{Cl}^-$  respectively.



**Fig. 4** Phosphorescence spectra of NAC and their complexes with heavy metal ions in ethanol at 77 K;  $[\text{NAC}] = 2 \times 10^{-4}$  mol/L,  $[\text{Metal ion}] = 1 \times 10^{-3}$  mol/L, excitation wavelength  $\lambda_{\text{ex}} = 320$  nm. The counter ions for  $\text{Ag}^+$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  are  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$  and  $\text{Cl}^-$  respectively.

### *Energy transfer from naphthalene chromophore to an inner transition-metal cation*

In contrast to alkali-metal ions and heavy-metal ions studied above, the lanthanide cation  $\text{Eu}^{3+}$  quenches both fluorescence and phosphorescence of NAC. The fluorescence quenching (Fig. 3) is understood in terms of heavy-atom effect. Although the bonding interactions between the nitrogen lone pair electrons of NAC and  $\text{Eu}^{3+}$  may enhance the fluorescence, the heavy-atom effect, which increases the quantum yield of the intersystem crossing of the naphthalene chromophore, is even more important in this case. As a result, the fluorescence intensity is reduced. Fig. 5 shows the phosphorescence spectra of NAC in ethanol glass in the presence of  $\text{Eu}^{3+}$



**Fig. 5** Phosphorescence spectra of NAC and its complex with  $\text{Eu}^{3+}$  in ethanol glass at 77 K with excitation at 320 nm;  $[\text{NAC}] = 2 \times 10^{-4}$  mol/L,  $[\text{Eu}(\text{NO}_3)_3] = 1 \times 10^{-3}$  mol/L. (a) Phosphorescence spectrum of NAC in the absence of  $\text{Eu}^{3+}$ ; (b) phosphorescence spectrum of NAC and fluorescence spectrum of  $\text{Eu}^{3+}$  for the solution of NAC and  $\text{Eu}^{3+}$ ; (c) fluorescence spectrum of  $\text{Eu}^{3+}$  in the absence of NAC.

by selective excitation of the naphthalene moiety at 320 nm. As the phosphorescence of NAC is quenched upon complexation with  $\text{Eu}^{3+}$ , the emission of  $\text{Eu}^{3+}$  with maxima at 593 and 619 nm is concomitantly observed. In a control experiment, excitation of  $\text{Eu}^{3+}$  in ethanol glass under identical conditions but in the absence of NAC led to no emission from  $\text{Eu}^{3+}$ . Obviously energy transfer from the naphthalene chromophore to  $\text{Eu}^{3+}$  occurred. Much elegant works have proved that in the complexes of organic hosts with lanthanide cation  $\text{Eu}^{3+}$  the

excitation energy of the ligands may efficiently be transferred to the cation, resulting in the luminescence of the latter.<sup>22,23</sup> The intramolecular energy transfer mechanism has been established.<sup>24-26</sup> The ligand absorbs energy and undergoes intersystem crossing to the lowest triplet state. The ion enhances the intersystem crossing of the ligand owing to the heavy-atom effect. Thus, the fluorescence of the ligand is quenched, and the quantum yield of the triplet state is increased. Then, the ligand triplet energy is transferred to the emitting state of the ion, and enhanced luminescence from the ion is observed. It is believed that in the complex of NAC with  $\text{Eu}^{3+}$ , the bonding interactions between the nitrogen lone pair electrons and  $\text{Eu}^{3+}$ , the heavy-atom effect, and the triplet energy transfer, all of the three processes are operative.

## Conclusions

It is shown that NAC forms complexes with the cations of alkali metal, heavy-metal and inner-transition-metal. Upon complexation, light-metal ions interact with the nitrogen lone pair electrons of NAC and inhibit the photoinduced intramolecular electron transfer from the nitrogen lone pair to the singlet excited state of the naphthalene chromophore, thus enhancing the fluorescence and phosphorescence quantum yield of the later. Heavy-metal ions show dual effects on the emission of NAC: the bonding with the nitrogen lone pairs increases the fluorescence, while the heavy-atom effect reduces the fluorescence quantum yield and enhances the phosphorescence. As a result, the fluorescence of the chromophore can be either enhanced (as in the case of  $\text{Rb}^+$  and  $\text{Cs}^+$ ) or quenched (as in the case of  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Ag}^+$ ). However, the phosphorescence is always enhanced significantly by complexation with heavy-metal ions. In the case of  $\text{Eu}^{3+}$ , energy transfer from triplet naphthalene chromophore to  $\text{Eu}^{3+}$  results in the decrease in phosphorescence of naphthalene. The enhanced phosphorescence of NAC by the complexation of heavy-metal ions could be used to design potential molecular photonic devices and chemosensors.

## Experimental

### *Instruments and materials*

$^1\text{H}$  NMR spectra were recorded on a BRUKER

DXP-400 spectrometer with TMS as an internal standard. IR spectra were obtained by using a Perking-Elmer Spectrum BX FT-IR System spectrometer. FAB MS spectra were obtained on a VG ZAB-HS (UK) Organic Mass spectrometer. Element analyses were performed by a HERAEUS CHN-RAPID instrument. Time-resolved fluorescence measurements were carried out with a HORIBA NAES-1100 time-resolved spectrofluorometer. Cyclic voltammetry experiments was performed on an EG&G PAR-283 Potentiostat with model 270 electrochemical software.

Spectral-grade alkali-metal chlorides, silver nitrate, lead perchlorate and mercury chloride were used without purification for emission spectrum measurements. Absolute ethanol was treated with sodium before use. Europium nitrate was prepared from europium oxide.

### *Fluorescence and phosphorescence measurements*

UV-VIS spectra of the compound were measured with a Perking Elmer Lambda 20 UV-VIS spectrometer. The emission and excitation spectra were detected in a Hitachi F-4500 Fluorescence spectrophotometer. Time-resolved fluorescence measurements were carried out with a HORIBA NAES-1100 time-resolved spectrofluorometer, operating on the single-photon counting principle, with appropriate deconvolution-fit programs.

The solution of NAC in ethanol in the presence of a metal salt was prepared. The samples were purged with nitrogen for at least 30 min before measurements. The fluorescence spectra were recorded at room temperature, while the phosphorescence spectra at 77 K. The excitation wavelength was either 280 nm or 320 nm. The spectra were fully corrected for instrumental response.

### *Cyclic voltammetry measurements*

The reduction potential of HEN was measured by cyclic voltammetry method. The measurements were carried out in acetonitrile solution by a platinum electrode (0.5 mm diameter) as working electrode. A platinum wire and a  $\text{Ag}/\text{AgCl}$  electrode were used as counter and reference electrodes, respectively. The concentration of HEN was  $1 \times 10^{-4}$  mol/L.

### *Synthesis of NAC*

NAC was synthesized by three steps; 2,3-bis(2-

hydroxyethoxyl) naphthalene was prepared and reacted with tosyl chloride to give the ditosylate, then the ditosylate reacted with diethanolamine to yield NAC.

**2,3-Bis(2-hydroxyethoxyl) naphthalene** This compound was prepared with a modified method reported in the literature.<sup>27</sup> To a solution of 2,3-dihydroxy-naphthalene (80 g, 0.5 mol) in 1.5 L of *n*-butanol, NaOH (40 g, 1.0 mol) was added under nitrogen atmosphere and the mixture was stirred and heated to reflux. 2-Chloroethanol (96.6 g, 1.2 mol) was added dropwise in 2 h, and the reaction was continued for 24 h. The reaction mixture was cooled and acidified with 10 mL of HCl during 6 h. The reaction mixture was filtered and the residual solid was washed with chloroform. The combined filtrate was concentrated by evaporation of the solvent under vacuum. A brownish oil was obtained which solidified on standing. This crude product was purified by column chromatography on silica gel with acetone/petroleum ether (*V/V* = 1/1) as eluent. The product was recrystallized from EtOH to give white crystal, yield 14%; m. p. 145–146 °C (lit.<sup>27</sup> 144–146 °C); <sup>1</sup>H NMR (CD<sub>3</sub>Cl) δ: 7.2–7.7 (m, 6H), 4.31 (t, *J* = 4.2 Hz, 4H), 4.12 (t, *J* = 4.3 Hz, 4H); IR (KBr) ν: 3304 (OH), 1487, 1509, 1601, 1629 (Ar, C = C), 1261 (= C—O—C) cm<sup>-1</sup>; MS *m/z* (%): 248 (M<sup>+</sup>, 43), 160 (100); Anal. calcd for C<sub>14</sub>H<sub>16</sub>O<sub>4</sub> · H<sub>2</sub>O: C 63.15, H 6.77; found C 63.42, H 6.83.

**2,3-Bis(2-hydroxyethoxyl) naphthalene ditosylate** 2,3-Bis(2-hydroxyethoxyl)-naphthalene (8.6 g, 0.035 mol) was dissolved into 40 mL of pyridine (dry). The solution was stirred and cooled below 0 °C, while tosyl chloride (14.7 g, 0.077 mol) in pyridine (dry, 20 mL) was added to the solution dropwise with stirring violently. The reaction temperature was kept below 2 °C. The reaction was remained at 4 °C for 12 h, then the reaction mixture was poured over ice and stirred. A gray-white solid (crude product) was obtained. Recrystallization from ethanol twice afforded white needle crystal, yield 88%; m. p. 110–112 °C (lit.<sup>27</sup> 111–112 °C); <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>) δ: 7.20–7.85 (m, 10H), 4.44 (t, *J* = 4.0 Hz, 4H), 4.34 (t, *J* = 4.1 Hz, 4H), 2.35 (s, 6H); IR (KBr) ν: 1629, 1598, 1509, 1486, 1458 (Ar, C = C), 1360, 1177 (SO<sub>2</sub>), 1256 (= C—O—C) cm<sup>-1</sup>; MS *m/z* (%): 556 (M<sup>+</sup>, 9), 199 (100); Anal. calcd for C<sub>28</sub>H<sub>28</sub>O<sub>8</sub>S<sub>2</sub>: C 60.43, H 5.04, S 11.51; found C 60.38, H 5.03, S 11.54.

**2,3-Naphtho-10-monoaza-15-crown-5 (NAC)**

Diethanolamine (8.4 g, 80 mmol) and sodium (3.3 g, 143 mmol) were added into 120 mL of *t*-butanol. The mixture was stirred and heated to 50–55 °C under nitrogen. After sodium was dissolved completely, a solution of 2,3-bis(2-hydroxyethoxyl) naphthalene ditosylate (19.02 g, 60 mmol) in 50 mL of dioxane was added during 3 h, and the reaction was continued for 6 h. The mixture was cooled to room temperature, and filtered. The residual solid was washed with chloroform. The filtrate was combined. The solvent was removed under vacuum. A brown yellow solid was obtained. The crude product was purified by column chromatography on silica gel with chloroform-methanol (*V/V* = 20/1) as eluent. Recrystallization from acetone-petroleum ether (30–60 °C) (*V/V* = 1/1) gave a white crystal, yield 34%; m. p. 167–169 °C; <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>) δ: 7.22–7.69 (m, 6H), 4.17 (t, *J* = 3.5 Hz, 4H), 3.86 (t, *J* = 3.8 Hz, 4H), 3.67 (t, *J* = 4.3 Hz, 4H), 2.70 (t, *J* = 4.3 Hz, 4H); IR (KBr) ν: 3317 (NH), 2874 (CH<sub>2</sub>), 1628, 1600, 1508, 1485, 1449 (Ar, C = C), 1255 (= C—O—C) cm<sup>-1</sup>; FAB MS *m/z* (%): 318 (M<sup>+</sup> + 1, 39); Anal. calcd for C<sub>18</sub>H<sub>23</sub>NO<sub>4</sub>: C 68.14, H 7.25, N 4.42, O 20.19; found C 68.22, H 7.31, N 4.15, O 21.45.

## References

- Desvergne, J.-P.; Czarnik, A. W. *Chemosensor of Ion and Molecular Recognition*, NATO ASI Series, Series C, Vol. 492, Kluwer Academic Press, Dordrecht, The Netherlands, **1997**.
- De Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515.
- De Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; McCoy, C. P. *Chem. Commun.* **1996**, 2399.
- Iwata, S.; Tanaka, K. *J. Chem. Soc., Chem. Commun.* **1995**, 1491.
- Ghosh, P.; Bharadwaj, P. K.; Mandal, S.; Ghosh, S. *J. Am. Chem. Soc.* **1996**, *118*, 1553.
- Ghosh, P.; Parimal, K.; Bharadwaj, P. K.; Ro, J.; Ghosh, S. *J. Am. Chem. Soc.* **1997**, *119*, 11903.
- Czarnik, A. W. *Acc. Chem. Res.* **1994**, *27*, 302.
- De Silva, A. P.; Gunaratne, H. Q. N.; McVeigh, C.; Maguire, G. E. M.; Maxwell, P. R. S.; Harlon, E. *Chem. Commun.* **1996**, 2191.
- De Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Nieuwenhuizen, M. *Chem. Commun.* **1996**, 1967.
- Fabbrizzi, L.; Poggi, A. *Chem. Soc. Rev.* **1995**, 197.

- 11 Tung, C.-H.; Zhang, H.-P.; Li, Y.; Cao, H.; Tanimoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 5348.
- 12 Fox, M. A.; Chanon, M. *Photoinduced Electron Transfer*, Elsevier, Amsterdam, **1988**.
- 13 Turro, N. J. *Modern Molecular Photochemistry*, Benjamin/Cummings Publishing Co., Inc., **1978**.
- 14 Ghosh, S.; Petrin, M.; Maki, A. H.; Sousa, L. R. *J. Chem. Phys.* **1987**, *87*, 4315.
- 15 Ghosh, S.; Petrin, M.; Maki, A. H.; Sousa, L. R. *J. Chem. Phys.* **1988**, *88*, 2913.
- 16 Bhattacharyya, S.; Sousa, L. R.; Ghosh, S. *Chem. Phys. Lett.* **1997**, *269*, 314.
- 17 Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.
- 18 Weller, A. Z. *Phys. Chem. Neue Folge* **1982**, *133*, 93.
- 19 Grellman, K. H.; Watkins, A. R.; Weller, A. J. *Phys. Chem.* **1972**, *76*, 3132.
- 20 Meites, L.; Zuman, P. *CRC Handbook Series in Organic Electrochemistry*, Vol. 1, CRC Press. Inc. **1976**, p. 96.
- 21 Webber, E. *Topics in Current Chemistry*, Springer-Verlag, Berlin, **1987**, Vol. 140; **1988**, Vol. 149.
- 22 Tung, C.-H.; Wu, L.-Z. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1381.
- 23 Bunzi, J. C.; Choppin, R. *Lanthanide Probes in life, Chemical and Earth Sciences*, Elsevier, Amsterdam, **1989**.
- 24 Takalo, H.; Hanninen, E.; Kankare, J. *Helv. Chim. Acta* **1993**, *76*, 877.
- 25 Mukkala, V.-M.; Helenius, M.; Hemmila, I.; Kankare, J.; Takalo, H. *Helv. Chim. Acta* **1993**, *76*, 1361.
- 26 Hemmila, I.; Mukkala, V.-M.; Latva, M.; Kiiholna, P. *J. Biochem. Biophys. Methods* **1993**, *26*, 283.
- 27 Czech, B.; Czech, A.; Bartsch, R. A. *Org. Prep. Proced. Int.* **1983**, *15*, 349.

(E0105146 LI, L. T.; ZHENG, G. C.)