

## Syntheses and Crystal Structures of Anthracene-Attached and Anthracene-Bridged NO<sub>2</sub>S<sub>2</sub>-Macrocycles as Fluoroionophores

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Fluorescent chemosensors have received considerable attention due to their potential applications in detection and quantification of the species over many fields.<sup>1-3</sup> In their protocols, the fluoroionophores have been prepared by coupling binding units (receptor part) and signaling units for the transduction of the binding event (input signal) into an observable output signal. Owing to their selective complexation with metal ions as well as great structural variety, macrocyclic ligands make them ideal candidates for the receptor part in the fluoroionophores.<sup>4-7</sup> In this regard, many efforts have been devoted to the development of new fluorescent macrocycles.

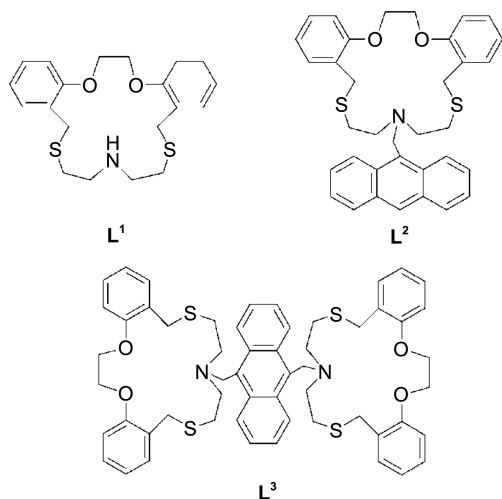
In the view of the receptor part, several NO<sub>2</sub>S<sub>2</sub> macrocycles involving **L**<sup>1</sup> that show an affinity for Hg<sup>2+</sup> and bind to this cation in both an exo- or endocyclic manner were reported by us<sup>8</sup> and another group.<sup>9</sup> Based on this results, we have investigated the *N*-azo-coupled analogue, which shows Hg<sup>2+</sup> selectivity; with the color of the Hg<sup>2+</sup> complex also controlled by the nature of the anion present.<sup>10</sup> We have also been involved in a program of preparing single and linked macrocycles with mixed donor sets exhibiting high selectivity for heavy metal ions.<sup>8,11</sup> For instance, we have reported the synthesis and structures for soft metal complexes of mono and linked macrocycles based on **L**<sup>1</sup> and structurally characterized.<sup>8,12</sup>

As an extension of our previous studies, we have been interested in the mono and di-linked macrocycles with the mixed-donor set to develop chemosensors for thiophilic metal species. As a preliminary work, we herein report the synthesis and characterization of the anthracene-attached (**L**<sup>2</sup>) and anthracene-bridged (**L**<sup>3</sup>) NO<sub>2</sub>S<sub>2</sub>-macrocycles of the parent NO<sub>2</sub>S<sub>2</sub> macrocycle **L**<sup>1</sup>.

### Experimental Section

**General.** All commercial reagents including solvents were of analytical reagent grade where available. NMR spectra were recorded on a Bruker DRX-500 spectrometer (500 MHz) and the mass spectra were obtained on a JEOL JMS-700 spectrometer at the Central Laboratory of Gyeongsang National University, respectively. The UV-vis absorption spectra were recorded either with a Varian Cary 5E and Scinco S-3100 spectrophotometer. Infrared spectra were measured with a Mattson Genesis Series FT-IR spectrophotometer.

**Synthesis of **L**<sup>2</sup>.** A solution of corresponding 9-(chloromethyl)anthracene in acetonitrile was added dropwise to a refluxing suspension of **L**<sup>1</sup> and potassium carbonate in acetonitrile. The reaction mixture was maintained at reflux condition for additional 24 h, allowed to cool to room temperature, then filtered. The filtrate was evaporated and the residue was partitioned between water and dichloromethane. The aqueous phase was separated and extracted with two further portions of dichloromethane. The combined organic phases were dried with anhydrous sodium sulfate and the solution then evaporated to dryness. The crude product chromatographed through silica gel. Yield: 35%. mp 173-175 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 2.49 (dd, 4H, *J* = 6.09 Hz, *J* = 7.92 Hz, SCH<sub>2</sub>CH<sub>2</sub>), 2.65 (dd, 4H, *J* = 7.25 Hz, NCH<sub>2</sub>CH<sub>2</sub>), 3.71 (s, 4H, ArCH<sub>2</sub>), 4.24 (s, 4H, CH<sub>2</sub>O), 4.37 (s, 2H, NCH<sub>2</sub>-anthracene), 6.77-7.23 (m, 8H, aromatic), 7.86-8.31 (m, 9H, anthracene). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 28.7, 29.3, 50.2, 52.9, 66.2, 75.8, 76.0, 76.3, 110.4, 120.2, 123.8, 124.0, 126.9, 127.0, 128.0, 129.5, 130.3, 130.4. HRMS (*m/z*) calcd. for C<sub>35</sub>H<sub>35</sub>NO<sub>2</sub>S<sub>2</sub>: 565.2109; found 565.2112.



**Synthesis of  $L^3$ .** A solution of corresponding 9,10-bis(bromomethyl)anthracene in acetonitrile was added dropwise to a refluxing suspension of  $L^1$  and potassium carbonate in acetonitrile. The reaction mixture was maintained at reflux condition for additional 24 h, allowed to cool to room temperature, then filtered. The filtrate was evaporated and the residue was partitioned between water and dichloromethane. The aqueous phase was separated and extracted with two further portions of dichloromethane. The combined organic phases were dried with anhydrous sodium sulfate and the solution then evaporated to dryness. The crude product chromatographed through silica gel. Yield: 25%. mp 176-179 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  2.60 (dd, 8H,  $J = 3$  Hz,  $J = 5.1$  Hz,  $\text{SCH}_2\text{CH}_2$ ), 2.74 (dd, 8H,  $J = 3$  Hz,  $J = 5.1$  Hz,  $\text{NCH}_2\text{CH}_2$ ), 3.82 (s, 8H, Ar $\text{CH}_2\text{S}$ ), 4.38 (s, 8H,  $\text{CH}_2\text{O}$ ), 4.46 (s, 4H,  $\text{NCH}_2$ -anthracene), 6.93-7.34 (m, 16H, aromatic) 7.40-8.42 (m, 8H, anthracene).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ): 29.5, 30.2, 51.2, 53.7, 67.1, 111.3, 121.1, 124.8, 125.4, 127.8, 130.3, 130.4, 130.8, 148.2, 156.2. MS (FAB) calcd.  $m/z = 952.3$ ; found 953.4 (M+1)

**Crystallography.** A crystal suitable for X-ray diffraction was mounted on a Bruker SMART diffractometer equipped with a graphite monochromated Mo  $K\alpha$  ( $\lambda = 0.71073$  Å) radiation source and a CCD detector and 45 frames of two-dimensional diffraction images were collected and processed to deduce the cell parameters and orientation matrix. A total of 7114 ( $L^2$ ) and 5306 ( $L^3$ ) frames of two-dimensional diffraction images were collected, each of which was measured for 20 sec. The frame data were processed to give structure factors by the program SAINT.<sup>13</sup> The intensity data were corrected for Lorentz and polarization effects. The structures were solved by a combination of the direct method and the difference Fourier methods provided by the program package SHELXTL,<sup>14</sup> and refined using a full matrix least square against  $F^2$  for all data. All the non-H

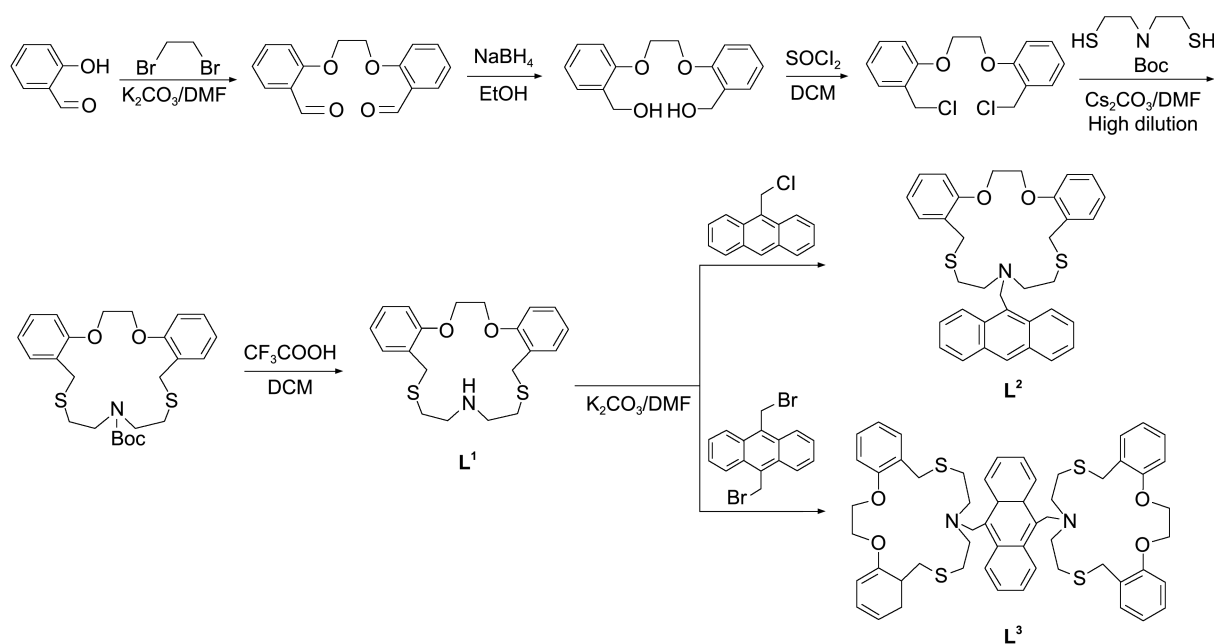
atoms were refined anisotropically. All hydrogen atoms were included in calculated positions with isotropic thermal parameters 1.2 times those of attached atoms. Crystallographic data are summarized in Table 1.

## Results and Discussion

$L^1$  was prepared according to our previous method.<sup>8</sup> Reaction of  $L^1$  with 9-chloromethylanthracene afforded the desired fluorescence macrocycle  $L^2$ . The linked ligand  $L^3$  was prepared from the parallel reaction with 9,10-bis-

**Table 1.** Crystal data and structural refinement for  $L^2$  and  $L^3$

	$L^2$	$L^3$
Formula	$\text{C}_{35}\text{H}_{35}\text{NO}_2\text{S}_2$	$\text{C}_{56}\text{H}_{60}\text{N}_2\text{O}_4\text{S}_4$
$M$	565.76	953.3
T/K	293(2)	293(2)
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P-1$
$a/\text{Å}$	14.781(3)	8.907(2)
$b/\text{Å}$	12.098(2)	9.577(2)
$c/\text{Å}$	18.233(3)	15.860(3)
$\alpha^\circ$		89.61(3)
$\beta^\circ$	112.446(4)	80.10(3)
$\gamma^\circ$		65.85(3)
$V/\text{Å}^3$	3013.4(9)	1213.1(4)
$Z$	4	1
Density (calcd)	1.247 $\text{Mg}/\text{m}^3$	1.305 $\text{Mg}/\text{m}^3$
Crystal size/mm	$0.2 \times 0.4 \times 0.4$	$0.2 \times 0.1 \times 0.1$
Reflections collected	19109	7682
Independent reflections	7114	5306
Goodness-of-fit on $F^2$	0.920	0.775
Final $R_1$ , $wR_2$ [ $I > 2\sigma(I)$ ]	0.0582, 0.1331	0.0830, 0.1635
(all data)	0.2162, 0.2091	0.3149, 0.2355



**Scheme 1.** Synthetic route to  $L^2$  and  $L^3$ .

(bromomethyl)anthracene in reasonable yield (Scheme 1). The target compounds were purified by silica-gel flash column chromatography in good yields. Their  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra exhibit characteristic singlets at 4.37 ( $\text{L}^2$ ), 4.46 ( $\text{L}^3$ ), and 52.9 ( $\text{L}^2$ ), 53.7 ( $\text{L}^3$ ) ppm, respectively, arising from the each methylene proton between *tert*-N and anthracene unit.

The structures of the target macrocycles  $\text{L}^2$  and  $\text{L}^3$  were also characterized in solid state by X-ray crystallography. The single crystals suitable for X-ray analysis were grown by slow evaporation of dichloromethane ( $\text{L}^2$ ) and ethyl-acetate/hexane ( $\text{L}^3$ ) solutions at room temperature. In the crystal of  $\text{L}^2$ , the macrocyclic ring is twisted with the two torsion angles between the S and N donors indicating a propensity for each linkage to adopt an *anti-gauche* conformation (Fig. 1). The anthracene ring is essentially planar but overall structure of the molecule is bent because of flexible nature of *N*-anthracenylmethyl group. As expected, two O atoms are oriented endodentate while two S atoms are arranged exodentate with respect to the ring cavity. The sulfur-to-sulfur distance in the ring is 6.331 Å.

In the crystal of  $\text{L}^3$ , there is an inversion center and the macrocyclic ring is considerably twisted and bent (Fig. 2). Unlike  $\text{L}^2$ , the two torsion angles between the S and N donors show an anti-anti arrangement. Accordingly, in this case, the sulfur-to-sulfur distance (7.006 Å) in the ring is larger than that of  $\text{L}^2$ . Similarly, the O and S atoms are oriented endo- and exodentate, respectively, to the ring cavity. The distance between two macrocyclic cavities is about 12.2 Å.

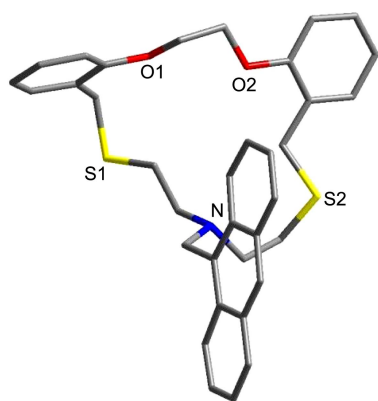


Figure 1. Crystal structure of  $\text{L}^2$ .

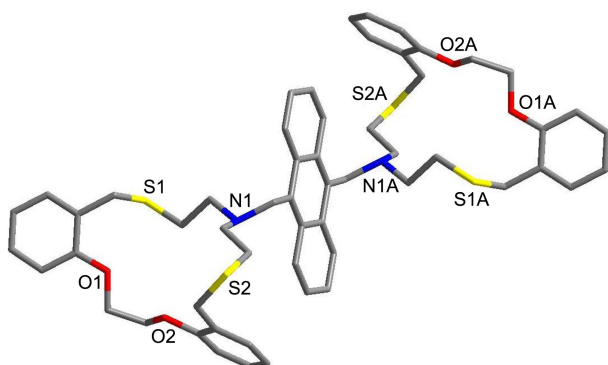


Figure 2. Crystal structure of  $\text{L}^3$ .

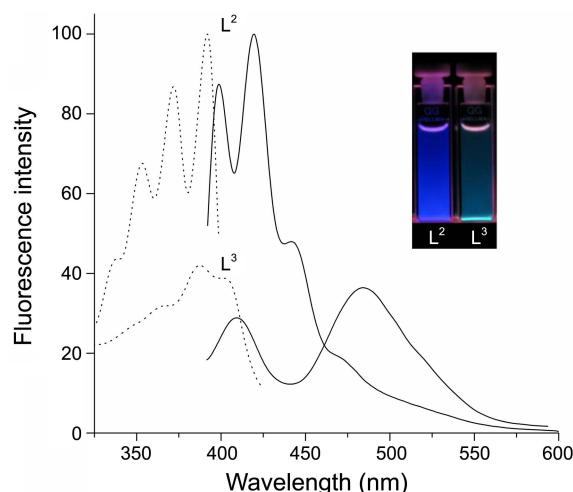


Figure 3. Excitation (dot) and emission (solid) spectra of  $\text{L}^2$  and  $\text{L}^3$  in acetonitrile.

Fluorescence behaviors of the proposed fluoroionophores were examined in solution state. First, the absorption and fluorescence spectra for  $\text{L}^2$  and  $\text{L}^3$  were measured in acetonitrile (Fig. 3). The excitation and emission spectra of  $\text{L}^2$  present the typical pattern of the anthracene,<sup>1</sup> with structured bands in the 320-400 and 380-480 nm regions, respectively. Those of  $\text{L}^3$ , however, show longer wave shift and fluorescence quenching, which could be due to the nonbonding electron pairs of the *tert*-N atoms participating in nonradiative quenching, such as intersystem crossing.<sup>15</sup>

As a preliminary tool, the cation sensing as fluorescent sensors toward metal ions (50 equiv) was tested for  $\text{L}^2$  and  $\text{L}^3$  (excitation at 368 nm). The fluorescent responses to diverse metal ions as perchlorate forms under same conditions are shown in Figure 4. For  $\text{L}^2$ , the changes of  $\lambda_{\text{em}}$  for each added metal ion were negligible, indicating no metal ions used influence the HOMO and LUMO levels in each ligand.

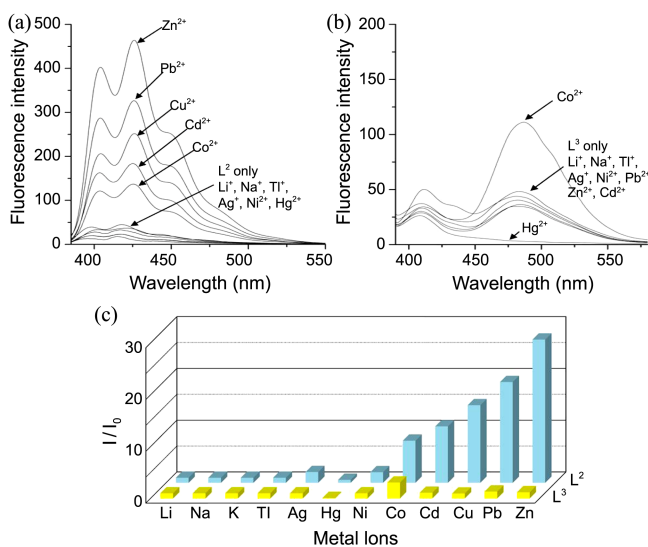


Figure 4. Fluorescence spectra of (a)  $\text{L}^2$  and (b)  $\text{L}^3$  in the presence of the metal perchlorates, and (c) normalized intensity ( $I/I_0$ ) in acetonitrile.

In this case, we found that the fluorescence intensity was enhanced by several divalent cations in the order  $\text{Zn}^{2+} > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Co}^{2+}$  suggesting, at least, the efficient binding of these cations toward  $\text{L}^2$ . Accordingly, the normalized intensity ( $I/I_0$ ) due to the maximum chelation enhanced fluorescence (CHEF) effect (ON state) was observed by  $\text{Zn}^{2+}$  (28-fold increase, Fig. 4(c)). Unlike  $\text{L}^2$ , the addition of  $\text{Hg}^{2+}$  resulted in the fluorescence quenching (OFF state) and no or less influences on the fluorescence intensity were shown by other metal ions except  $\text{Co}^{2+}$  whose intensity increase is similar to the case of  $\text{L}^2$ .

Our repeated effort to obtain the crystal structure of the corresponding complexes was not successful. Due to the lack of the structural information for the related complexes, the conclusive evidence for the observed sensing behaviors could not be well drawn. In our previous works for  $\text{L}^1$ -based sensor molecules, however, the parent macrocycle  $\text{L}^1$  and its N-modified macrocyclic analogues commonly show high selectivity for  $\text{Hg}^{2+}$  both in solution and solid states.<sup>10,11</sup> On the basis of these results, the observed maximum turn-off quenching of  $\text{L}^3$  induced by  $\text{Hg}^{2+}$  could be explained by the stronger coordination affinity than other system. Further studies on complexation behaviors as well as the information on structural/function relationships are in progress.

In summary, anthracene-attached ( $\text{L}^2$ ) and anthracene-bridged ( $\text{L}^3$ )  $\text{NO}_2\text{S}_2$ -macrocycles were synthesized by the reactions of their parent  $\text{NO}_2\text{S}_2$ -macrocycle  $\text{L}^1$  with 9-chloromethylanthracene and 9,10-bis(bromomethyl)anthracene, respectively. Moreover, the crystal structures of the proposed fluoroionophores were confirmed by X-ray crystallography. In a preliminary fluorescence study,  $\text{L}^2$  and  $\text{L}^3$  show intense structural emission bands in acetonitrile. Upon addition of metal cations,  $\text{L}^2$  exhibits a highest CHEF effect (28-fold, TURN-ON) in the presence of  $\text{Zn}^{2+}$ . On the other hand, the linked analogue  $\text{L}^3$  shows a maximum quenching effect (TURN-OFF) for  $\text{Hg}^{2+}$ .

**Supplementary Materials.** CCDC 252327 and 813925 contain the supplementary crystallographic data, respectively. These data can be obtained free of charge *via* www.ccdc.

cam.ac.uk/data\_request/cif, by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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