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Novel Optical/Electrochemical Selective 1,2,3-Triazole Ring-Appended Chemosensor for the Al^{3+} Ion

Sang Hoon Kim,[†] Hong Seok Choi,[‡] Joohoon Kim,[*,‡] Suk Joong Lee,[†] Duong Tuan Quang,[†] and Jong Seung Kim[*,†]

Department of Chemistry, Korea University, Seoul 136-701, Korea, and Department of Chemistry and Research Institute for Basic Sciences, Kyung Hee University, Seoul 130-701, Korea

jkim94@khu.ac.kr; jongskim@korea.ac.kr

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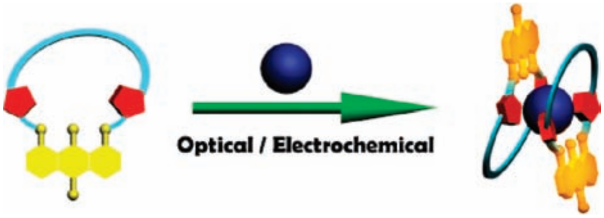
ABSTRACT



A chemosensor (1) bearing a 1,2,3-triazole ring spacer was synthesized for the selective detection of Al^{3+} with respect to dual optical and electrochemical changing events. The addition of Al^{3+} ions to 1 induced a significant change in fluorescence intensity, attributable to ICT and CHEF effects from the 1,2,3-triazole ring. The electrochemical behavior of 1 in the presence of the Al^{3+} ion was significantly altered compared with those of the other metal cations tested.

Aluminum is the most abundant (8.3% by weight) metallic element and the third most abundant of all elements (after oxygen and silicon). As such, it has been widely used in many industrial fields, including the manufacturing of cars and computers.[1] Conversely, the Al^{3+} ion has gained prominence through a possible biochemical link to Alzheimer's disease by way of its toxicity. Furthermore, it is known that 40% of the world's acidic soils is caused by aluminum toxicity.[2] Nevertheless, regarding detection of the Al^{3+} ion, only a few chemosensors have been reported thus far,[3] limited in their selectivity and sensitivity over other metal cations.

Anthraquinone has been utilized as a chemosensor for metal ions and anions given its high absorption coefficient and possibility of naked eye detection.[4] Moreover, it has been popular in electroanalytical chemistry since its quinone system showed two successive electron reduction steps

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[†] Korea University.

[‡] Kyung Hee University.

(1) (a) Barceló, J.; Poschenrieder, C. *Environ. Exp. Bot.* **2002**, *48*, 75–92. (b) Lakowicz, J. R. *Topics in Fluorescence Spectroscopy: Probe Design and Chemical Sensing*; Kluwer Academic Publishers: New York, 2002; Vol. 4. (c) 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*, 1515–1566. (d) Valeur, B.; Leray, I. *Coord. Chem. Rev.* **2000**, *205*, 3–40.

(2) (a) Flaten, T. P.; Ødegård, M. *Food Chem. Toxical.* **1988**, *26*, 959–960. (b) Ren, J.; Tian, H. *Sensors* **2007**, *7*, 3166–3178. (c) Yokel, R. A. *Neurotoxicology* **2000**, *21*, 813–828.

(3) (a) Kim, H. J.; Kim, S. H.; Quang, D. T.; Kim, J. H.; Suh, I.; Kim, J. S. *Bull. Korean Chem. Soc.* **2007**, *28*, 811–815. (b) Saari, L. A.; Seltz, W. R. *Anal. Chem.* **1983**, *55*, 667–670. (c) Arduini, M.; Felluga, F.; Mancin, F.; Rossi, P.; Tecilla, P.; Tonellato, U.; Valentinuzzi, N. *Chem. Commun.* **2003**, 1606–1607. (d) Lin, W.; Yuan, L.; Feng, J. *Eur. J. Org. Chem.* **2008**, *382*, 1–3825. (e) Othman, A. B.; Lee, J. W. Lee; Huh, Y.; Abidi, R.; Kim, J. S.; Vicens, J. *Tetrahedron* **2007**, *63*, 10793–10800. (f) Jeanson, A.; Be'reau, V. *Inorg. Chem. Commun.* **2006**, *9*, 13–17. (g) Jiang, C.; Tang, B.; Wang, R.; Yen, J. *Talanta* **1997**, *44*, 197–202. (h) Kim, J. S.; Lee, S. Y.; Yoon, J.; Vicens, J. *Chem. Commun.* **2009**, 4791–4802.

(4) (a) Zhu, L.; Khairutdinov, R. F.; Cape, J. L.; Hurst, J. K. *J. Am. Chem. Soc.* **2006**, *128*, 825–835. (b) Devaraj, S.; Saravanakumar, D.; Kandaswamy, M. *Tetrahedron Lett.* **2007**, *48*, 3077–3081. (c) Kadarkaraisamy, M.; Sykes, A. G. *Inorg. Chem.* **2006**, *45*, 779–786. (d) Ranyuk, E.; Douaihy, C. M.; Bessmertnykh, A.; Denat, F.; Averin, A.; Beletskaya, I.; Guilard, R. *Org. Lett.* **2009**, *11*, 987–990.

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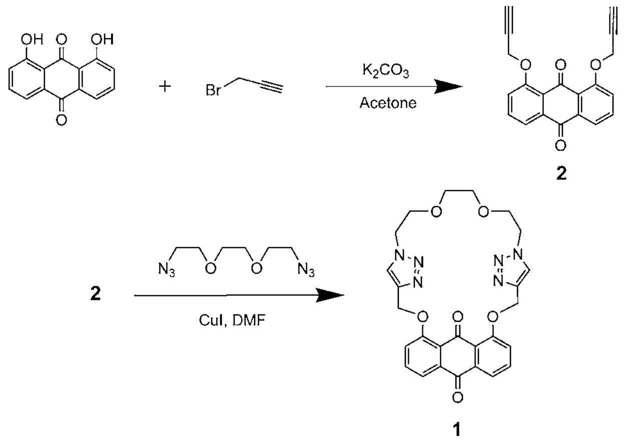
forming Q^{1-} and then Q^{2-}.[5] Therefore, the host molecule in connection with the anthraquinone moiety as a sensing unit might be useful for metal cation detection by means of the unique optical/electrochemical responses toward target analytes.

The development of the Cu(I)-catalyzed 1,3-dipolar cycloaddition of alkynes and azides (Click reaction) has provided a straightforward molecular linking strategy adopted in a wide range of synthetic applications.[6] The 1,2,3-triazole framework formed by the Click reaction was also utilized as binding sites for metal ions and anions.[6] Recently, Li and co-workers reported the synthesis of 1,2,3-triazole-modified calix[4]crowns as binding sites for alkali/transition metal ions.[7]

In this paper, we report the synthesis and optical/electrochemical behavior of the 1,2,3-triazole ring-appended chemosensor **1** toward various metal ions.

Compound **1** was synthesized in two steps as shown in Scheme 1. The reaction of 1,8-dihydroxyanthraquinone with 2.1 equiv of propargyl bromide and K_2CO_3 in acetone as a solvent afforded the desired 1,8-bis(prop-2-ynyloxy)anthraquinone (**2**) in moderate yield. The Cu(I)-catalyzed cycloaddition[8] of **2** with 1,2-bis(2-azidoethoxy)ethane gave **1** in 35% yield.

Scheme 1. Synthetic Route to **1**



The photophysical properties of **1** were investigated by monitoring absorption and fluorescence changes upon addition of the perchlorate salt of a wide range of cations in CH_3CN, including: Li^+, Na^+, K^+, Ag^+, Mg^{2+}, Ca^{2+}, Co^{2+}, Ba^{2+}, Sr^{2+}, Cu^{2+}, Hg^{2+}, Pb^{2+}, In^{3+}, Rb^+, Cd^{2+}, and Al^{3+}. The fluorescence and UV/vis changes are depicted in Figure 1(a) and Supporting Information (SI) Figure S6, respectively. Compound **1** showed an absorption band centered at 380 nm, corresponding to the anthraquinone moiety. Upon addition of the Al^{3+} ion, a new broad absorption band at the 500 nm region appeared. Interestingly, in the emission spectrum, the fluorescence intensity of **1** ($\Phi_F = 0.083$) increased remarkably at 557 nm ($\Phi_F = 0.463$) upon addition of the Al^{3+} ion, as shown in Figure 1(a).

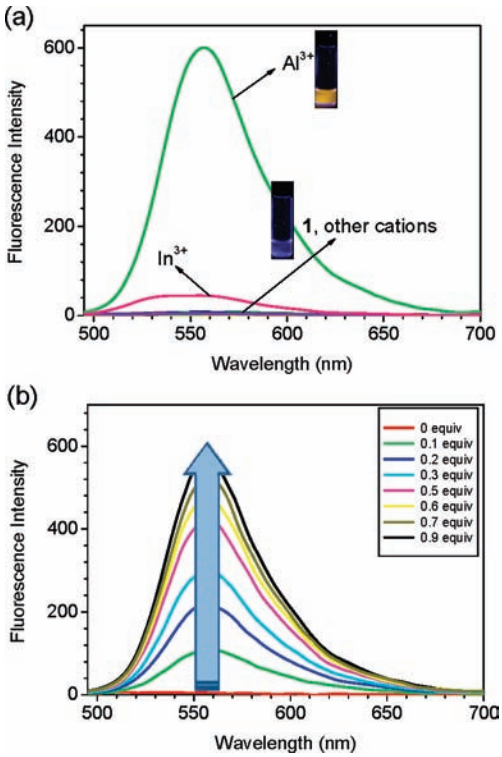


Figure 1. (a) Fluorescence spectra of **1** in CH_3CN (50 μM) upon addition of the ClO_4^- salt of: Li^+, Na^+, K^+, Ag^+, Mg^{2+}, Ca^{2+}, Co^{2+}, Ba^{2+}, Sr^{2+}, Cu^{2+}, Hg^{2+}, Pb^{2+}, In^{3+}, Rb^+, Cd^{2+}, and Al^{3+} (50 equiv). Photographs of the chemosensing responses (**1** and **1**·Al^{3+} under UV light). (b) Fluorescence spectra of **1** (50 μM) in CH_3CN upon the addition of the Al^{3+} ion (0, 0.1, 0.2, 0.3, 0.5, 0.6, 0.7, and 0.9 equiv) with an excitation at 478 nm.

Job plot and Benesi−Hildbrand plot experiments were carried out, with the results showing a 2:1 stoichiometry complexation between **1** and the Al^{3+} ion (Figure S5, SI). Figure 1(b) and Figure S7 (SI) give detailed fluorescence and absorption changes of **1** upon gradual addition of the Al^{3+} ion, from which the association constant (log K_a) of **1** for Al^{3+} was calculated to be 4.52.[9]

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(5) (a) Zon, A.; Palys, M.; Stojek, Z.; Sulowska, H.; Ossowski, T. *Electroanalysis* **2003**, *15*, 579–585. (b) Park, D. H.; Kang, S. O.; Lee, H.; Nam, K. C.; Jeon, S. *Bull. Korean Chem. Soc.* **2001**, *22*, 638–640.

(6) (a) Park, S. Y.; Yoon, J. H.; Hong, C. S.; Souane, R.; Kim, J. S.; Matthews, S. E.; Vicens, J. *J. Org. Chem.* **2008**, *73*, 8212–8218. (b) Suijkerbuijk, B. M. J. M.; Aerts, B. N. H.; Dijkstra, H. P.; Lutz, M.; Spek, A. L.; Koten, G.; Gebbink, R. J. M. K. *Dalton Trans.* **2007**, *22*, 1273–1276. (c) Chang, K.; Su, I.; Senthilvelan, A.; Chung, W. *Org. Lett.* **2007**, *9*, 3363–3366. (d) Haridas, V.; Lal, K.; Sharma, Y. K.; Upreti, S. *Org. Lett.* **2008**, *10*, 1645–1647. (e) Hung, H.; Cheng, C.; Ho, I.; Chung, W. *Tetrahedron Lett.* **2009**, *50*, 302–305. (f) Li, Y.; Flood, A. H. *Angew. Chem., Int. Ed.* **2008**, *47*, 2649–2652.

(7) Zhan, J.; Tian, D.; Li, H. *New J. Chem.* **2009**, *33*, 725–728.

(8) Megiatto, J. D.; Schuster, D. I. *J. Am. Chem. Soc.* **2008**, *130*, 12872–12873.

(9) (a) Lin, W.; Yuan, L.; Long, L.; Guo, C.; Feng, J. *Adv. Funct. Mater.* **2008**, *18*, 2366–2372. (b) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703–2707. (c) Mizyed, S.; Tarabsheh, H.; Marji, D. *Jordan J. Chem.* **2007**, *2*, 145–153. (d) Vosburgh, W. C.; Cooper, G. R. *J. Am. Chem. Soc.* **1941**, *63*, 437–442. (e) Kim, J. S.; Quang, D. T. *Chem. Rev.*

Additionally, experiments carried out to know the influence of concentration on sensing properties showed that at least 0.5 μM Al^{3+} ion could be detected in CH_3CN (Figure S12, SI).

The ^1H NMR spectra of **1** and **1**·Al^{3+} in CD_3CN were also recorded to verify the complexation mode of **1** toward the Al^{3+} ion, with spectral differences depicted in Figure 2. The signals of H_a, H_b, H_c, and H_e were downfield shifted by ca. 0.05 ppm, while the signals of the other protons remained nearly unchanged. These results are highly indicative of the Al^{3+} ion being bound to two triazole rings, as well as an anthraquinone unit, within a 2:1 complexation mode.

From all spectroscopic data, it can be concluded that metal binding to the carbonyl group in the anthraquinone leads to a red shift in the absorption band of **1** by ICT (intramolecular charge transfer).[10] Enhancement of the fluorescence intensity of **1** is presumably due to the metal binding to triazole rings followed by PET suppression, denoted as CHEF (chelation-enhanced fluorescence).[11] A plausible complexation mode is therefore depicted in Figure 2.

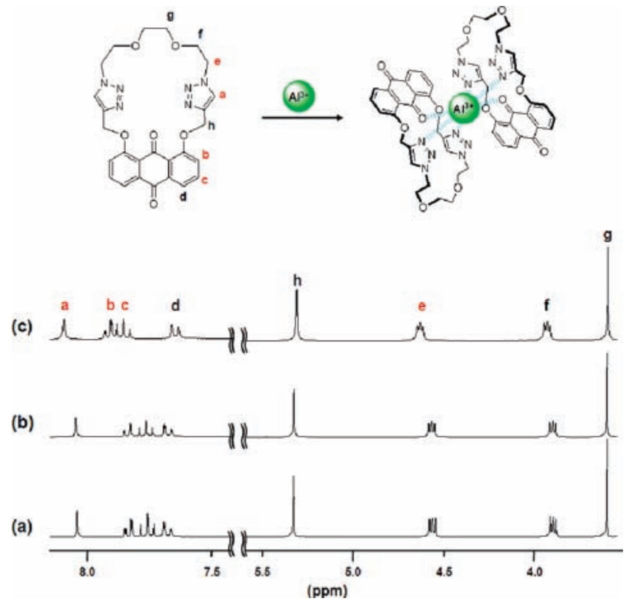

Figure 2. ^1H NMR titration spectra of **1** in CD_3CN in the presence of $Al(ClO_4)_3$ and its plausible binding mode. (a) **1** only, (b) **1** and 0.5 equiv of Al^{3+}, (c) **1** and 1.0 equiv of Al^{3+}.

To utilize **1** as an optical/electrochemical ion-selective chemosensor for Al^{3+}, competition experiments with many other metal cations were also carried out. Variations in the fluorescence and UV/vis spectra of **1** in the presence of various cations in CH_3CN, including Li^+, Na^+, K^+, Ag^+, Mg^{2+}, Ca^{2+}, Co^{2+}, Ba^{2+}, Sr^{2+}, Cu^{2+}, Hg^{2+}, Pb^{2+}, In^{3+}, Rb^+, and Cd^{2+} (50 equiv as ClO_4^- salts), are given in Figure 3 and Figure S8 (SI), respectively. There were insignificant changes in the fluorescence and absorption of **1**·Al^{3+} upon addition of most other competing metal cations, suggesting that **1** can be used as a selective chemosensor for the Al^{3+} ion.

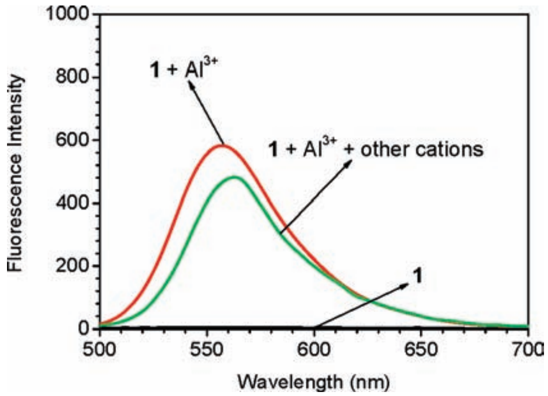

Figure 3. Fluorescence spectra of **1** (50.0 μM) in CH_3CN upon addition of 50 equiv of Al^{3+} in the presence of ClO_4^- salts of various cations. Excitation at 478 nm.

Electrochemical behaviors of **1** in the absence or presence of Al^{3+} in CH_3CN were investigated by differential pulse voltammetry (DPV). A differential pulse voltammogram of 0.2 mM free **1** (**1**:Al^{3+} = 1:0) is shown in Figure 4. Two well-defined cathodic peaks at −1.3 and −1.7 V were observed with free **1**, which correspond to two successive one-electron transfers to the anthraquinone moiety of **1**.[12] However, the electrochemical behavior of **1** in the presence of Al^{3+} was significantly altered. Figure 4 shows the changes that occurred in the voltammograms of **1** upon the addition of successive amounts of Al^{3+}. For a concentration ratio of **1**:Al^{3+} = 6:1, 4:1, and 2:1, three reduction waves were observed, one (near −1.3 V) corresponding to the first reduction of free **1** and two new waves (near −0.4 and −0.8 V) corresponding to the successive reductions of the **1**·Al^{3+} complex (2:1 complexation mode). Both new reduction peaks were positioned at more positive potentials than the corresponding peak of free **1**, reflecting strong **1**·Al^{3+} interactions and an increase in the complexation strength of reduced **1** to the Al^{3+} ion compared with the neutral species.[13] At a concentration ratio of **1**:Al^{3+} = 1:1, no reduction peak of free **1** could be observed (Figure 4), indicating a very small

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2007, *107*, 3780–3799.

(10) (a) Peng, X.; Du, J.; Fan, J.; Wang, J.; Wu, Y.; Zhao, J.; Sun, S.; Xu, T. *J. Am. Chem. Soc.* **2007**, *129*, 1500–1501. (b) Kim, H. J.; Kim, S. H.; Kim, J. H.; Anh, L. N.; Lee, J. H.; Lee, C.; Kim, J. S. *Tetrahedron Lett.* **2009**, *50*, 2782–2786. (c) Kim, H. N.; Lee, M. H.; Kim, H. J.; Kim, J. S.; Yoon, J. *Chem. Soc. Rev.* **2008**, *37*, 1465–1472.

(11) (a) Gunnlaugsson, T.; Lee, T. C.; Parkesh, R. *Org. Lett.* **2003**, *5*, 4065–4068. (b) Kim, J. S.; Noh, K. H.; Lee, S. H.; Kim, S. K.; Kim, S. K.; Yoon, J. *J. Org. Chem.* **2003**, *68*, 597–600. (c) Kim, J. S.; Shon, O. J.; Rim, J. A.; Kim, S. K.; Yoon, J. *J. Org. Chem.* **2002**, *67*, 2348–2351.

(12) (a) Gustowski, D. A.; Delgado, M.; Gatto, V. J.; Echegoyen, L.; Gokel, G. W. *J. Am. Chem. Soc.* **1986**, *108*, 7553–7560. (b) Chen, Z.; Schall, O. F.; Alcalá, M.; Li, Y.; Gokel, G. W.; Echegoyen, L. *J. Am. Chem. Soc.* **1992**, *114*, 444–451.

(13) (a) Miller, S. R.; Gustowski, D. A.; Chen, Z.; Gokel, G. W.; Echegoyen, L.; Kaifer, A. E. *Anal. Chem.* **1988**, *60*, 2021–2024. (b) Delgado, M.; Gustowski, D. A.; Yoo, H. K.; Gatto, V. J.; Gokel, G. W.; Echegoyen, L. *J. Am. Chem. Soc.* **1988**, *110*, 119–124.

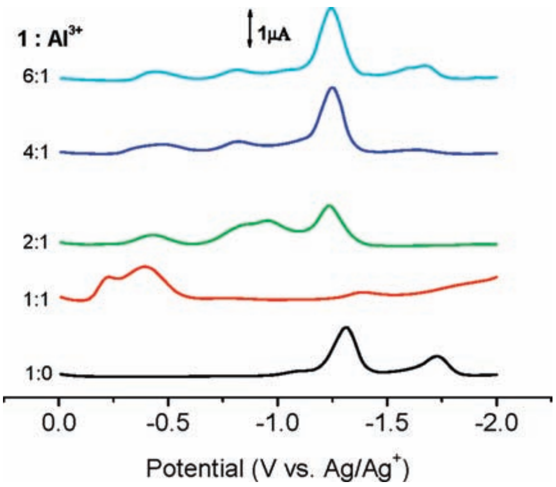

Figure 4. Differential pulse voltammograms of 0.2 mM **1** in the absence and presence of the Al^{3+} ions. Electrolyte: 0.1 M TBAP/CH_3CN. Pulse amplitude: 50 mV. The molar ratio of **1** to Al^{3+} (**1**:Al^{3+}) varied from 1:0 to 6:1.

amount of free **1** and its negligible reduction processes given the **1**:Al^{3+} complexation. It is worthy to note that an additional reduction peak at −0.2 V was observed on the voltammogram at a concentration ratio of **1**:Al^{3+} = 1:1. This is believed to result from the reduction of the **1**·Al^{3+} complex (1:1 complexation mode), which becomes significant as the concentration of **1** decreases in comparison to that of Al^{3+}. The relative intensity of the reduction peaks of free **1** disappeared progressively with a function of [Al^{3+}], indicating complexation of **1** with Al^{3+}. The electrochemical behaviors of **1** in the presence of alkali and alkaline earth metal ions were also investigated, and the results showed a weaker binding strength of **1** to metal ions other than Al^{3+} (Figures S9 and S10, SI). However, alkaline earth metal ions were strongly bound to **1** compared to the alkali metal ions, reflecting the interaction of alkaline earth metal ions with the 1,2,3-triazole ring system of **1**, in which the nitrogen atoms prefer to bind the alkaline earth metal ions to the alkali metal ions with regard to acid/base hardness.

In summary, a novel chemosensor bearing a 1,2,3-triazole ring spacer was synthesized and studied for its optical/electrochemical properties. The complexation of the Al^{3+} ion with **1** showed an enhanced fluorescence change at 556 nm, presumably due to a combinational effect of ICT and CHEF during the chelation of **1** toward the Al^{3+} ion by both the 1,2,3-triazole ring and carbonyl groups within a 2:1 complex mode. Furthermore, compound **1** showed significant changes in its electrochemical behavior upon addition of the Al^{3+} ion. Hence, **1** can be used as an optical/electrochemical sensor for the Al^{3+} ion.

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Supporting Information Available: Synthetic details, NMR copies, and additional spectra data. This material is available free of charge via the Internet at http://pubs.acs.org.

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