JOC Article

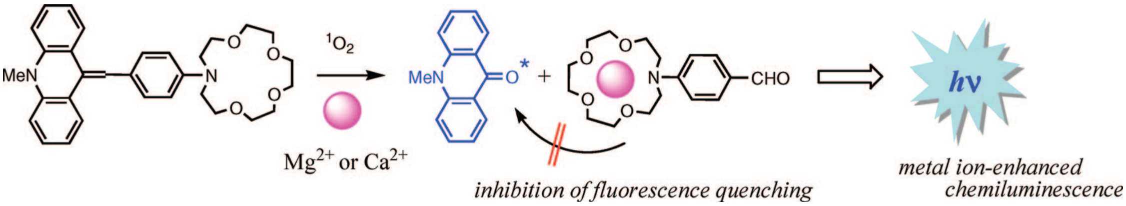
Toward a Chemiluminescent Molecular Device: Metal Ion-Enhanced Chemiluminescence of Benzylidenacridan with 15-Monoazacrown-5

Jiro Motoyoshiya,* Toshimitsu Tanaka, Motoki Kuroe, and Yoshinori Nishii

Department of Chemistry, Faculty of Textile Science and Technology, Shinshu University, Ueda, Nagano, 386-8567, Japan

jmotoyo@shinshu-u.ac.jp

Received July 23, 2008



The benzylidenacridans (**1a−d**) with one or more methoxy groups emit light from the excited *N*-methylacridone (NMA) when treated with a solution of sodium hypochlorite and alkaline hydrogen peroxide, in which a Hammett relationship with a negative ρ value was applied between the chemiluminescence quantum yields and the σ values. However, the dimethylamino group drastically inhibited the chemiluminescence in spite of its low σ value. While the compound (**2**) with 15-monoazacrown-5 also showed a very weak chemiluminescence upon treatment with tetrabutylammonium hydroxide and hydrogen peroxide in acetonitrile, the chemiluminescence was enhanced up to 20 times in efficiency when divalent metal cations, such as magnesium and calcium ions, were added. The chemiluminescence inhibition is proved to be due to the shortening of the fluorescence lifetime of NMA due to energy dissipation by the amino substituents, but the incorporation of calcium ion into the cavity of the azacrown significantly prolonged the lifetime. Thus, the possibility of metal ion sensing by a chemiluminescent molecular device is suggested.

Introduction

Chemiluminescence is a phenomenon in which an electronically excited molecule is generated during the chemical reaction and emits light as a visual output. Of significance is the application of chemiluminescence to analytical chemistry[1] as well as in the field of biotechnology if the target chemical species can be monitored as a light emission signal.[2] In spite of numerous reports of fluorescent devices for these purposes,[3] less attention has been paid to the chemiluminescent systems, whose greatest advantage is needless of an electric light source to prevent reduction of the sensitivity due to the background. To utilize the chemiluminescent reaction for molecular sensing, there are two categories of methods: Namely, the first is energy transfer chemiluminescence using suitable fluorescent devices and chemiluminescent molecules as the energy supplements that produces excitation of the fluorescent energy acceptors.[1] The second is the chemiluminescence device whose emission is modulated by the target molecule.[4] In this paper, we report the chemiluminescent system based on the latter concept, that is, suitable metal cations combine with the chemiluminescent molecules, resulting in an enhanced chemiluminescence intensity.

Since the early study by McCapra et al.,[5] chemiluminescence from the thermal decomposition of acridan dioxetanes generated by singlet oxygenation of several benzylidenacridans has been

---

(1) (a) Tsunoda, M.; Imai, K. *Anal. Chim. Acta* **2005**, *541*, 13–23. (b) Marquette, C. A.; Blum, L. J. *Anal. Bioanal. Chem.* **2006**, *385*, 546–554. (c) Fletcher, K. A.; Fakayode, S. O.; Lowry, M.; Tucker, S. A.; Neal, S. L.; Kimaru, I. W.; McCarroll, M. E.; Patonay, G.; Oldham, P. B.; Rusin, O.; Strongin, R. M.; Warner, I. M. *Anal. Chem.* **2006**, *78*, 4047–4068.

(2) Roda, A.; Guardigli, M.; Pasini, P.; Mirasoli, M.; Michelini, E.; Musiani, M. *Anal. Chim. Acta* **2005**, *541*, 25–35.

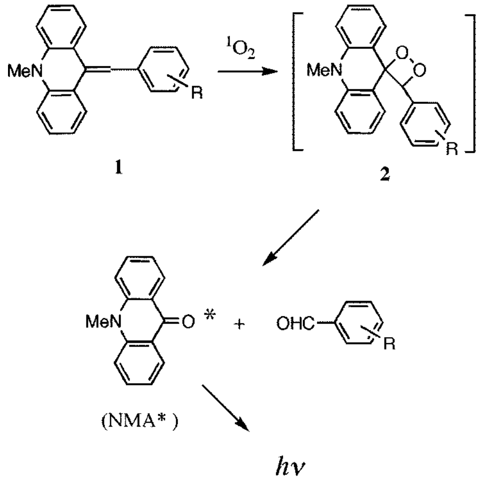
(3) (a) Xia, W.-S.; Schmehl, R. H.; Li, C.-J. *Chem. Commun.* **2000**, 695–696. (b) Gokel, G. W.; Leevy, W. M.; Weber, M. E. *Chem. Rev.* **2004**, *104*, 2723–2750. (c) Powe, A. M.; Fletcher, K. A.; St, N. N.; Lowry, M.; Neal, S.; McCarroll, M. E.; Oldham, P. B.; McGown, L. B.; Warner, I. M. *Anal. Chem.* **2004**, *76*, 4614–4634. (d) Zhang, M.; Yu, M.; Li, F.; Zhu, M.; Li, M.; Gao, Y.; Li., L.; Liu, Z.; Zhang, J.; Zhang, D.; Yi, T.; Huang, C. *J. Am. Chem. Soc.* **2007**, *129*, 10322–10323. (e) Koide, Y.; Urano, Y.; Kennmoku, S.; Kojima, H.; Nagano, T. *J. Am. Chem. Soc.* **2007**, *129*, 10324–10325.

(4) (a) Dodeigne, C.; Thunus, L.; Lejeune, R. *Talanta* **2000**, *51*, 415–439. (b) Okamoto, H.; Owari, M.; Kimura, M.; Satake, K. *Tetrahedron Lett.* **2001**, *42*, 7453–7455. (c) Okamoto, H.; Kimura, M. *Chem. Lett.* **2005**, *34*, 1452–1453.

(5) McCapra, F.; Beheshti, I.; Burford, A.; Hann, R. A.; Zaklika, K. A. *J. Chem. Soc., Chem Commun* **1977**, 944–946.

10.1021/jo801556p CCC: $40.75

SCHEME 1. Chemiluminescence Reaction of 9-Benzylidenacridans



occasionally investigated[6] and it is suggested that the unstable 1,2-dioxetanes were generated as the intermediates,[7] in which the corresponding aldehydes and the fluorescent *N*-methylacridone (NMA), the latter of which is the emitter, were formed as the decomposition products (Scheme 1). In this chemiluminescence reaction, the Hammett relationship with a negative ρ value is adopted between the σ values of the substituents on the benzylidene moieties and the chemiluminescence efficiency;[8] namely, the electron-donating substituents efficiently promote the chemiluminescence process. However, the dimethylamino group is the exception as it drastically inhibits the chemiluminescence.[9] The interesting feature of this chemiluminescence system encourages us to apply it to a new metal sensing system using the selective metal incorporating function of the azacrown ether. In this paper, we report the chemiluminescence behavior of the 9-benzylidene-10-methylacridans bearing 15-monoazacrown-5, in which the azacrown acts as a metal cation recognition site and the chemiluminescence efficiency is selectively enhanced in the presence of magnesium and calcium cations.

Results and Discussion

The benzylidenacridans used in the present study were prepared by the Horner–Wadsworth–Emmons reaction of 9-diethylphosphono-10-methylacridan and the corresponding aromatic aldehydes.[8] Their structures are shown in Chart 1.These benzylidenacridans were subjected to the chemiluminescence reaction by singlet oxygenation, using a combination of hydrogen peroxide and sodium hypochlorite in aqueous methanol as a singlet oxygen evolution system.[10] When **1a** was treated at a high concentration of the substances under these conditions, it emits a flash of blue light observable by the naked eye, whose chemiluminescence spectrum was in agreement with the fluorescence spectrum of NMA, indicating that the excited NMA was generated by this oxidation reaction. The total chemiluminescence quantum yield (Φ_{CL}) of **1a** under the optimized reaction conditions was estimated as 0.011 einstein/mol. A few other compounds with two or three methoxy groups (**1b**–**d**) also emit light, and an approximately linear relationship with the negative slope exists between the logarithm of their singlet excitation yields (Φ_S) and the sum of the Hammett σ values (Table 1 and Figure 1). On the contrary, the similar treatment of **1e** bearing a dimethylamino group gave an extremely weak chemiluminescence in spite of its small σ value, whose Φ_S was only 1/1300 compared to that of **1a**.

CHART 1. Structures of Benzylidenacridans Used in This Study

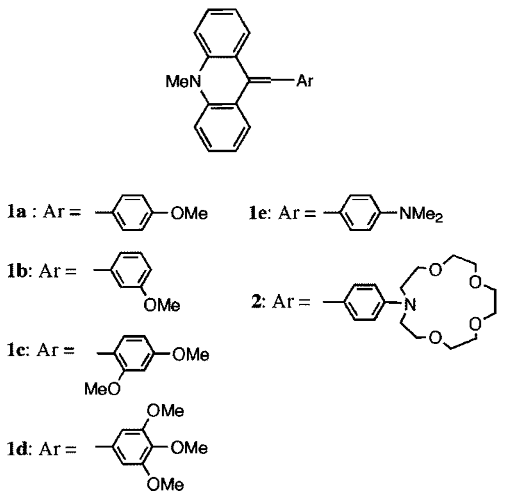


TABLE 1. Data of the Chemiluminescence Reaction of Benzylideneacridanes (1)

	R	$\Sigma\sigma$	$10^4\Phi_{CL}$[a]	Φ_r[b]	$10^4\Phi_S$[c]
1a	*p*-OMe	−0.27	110	0.91	130
1b	*m*-OMe	0.12	0.33	0.83	0.44
1c	2,4-(OMe)$_2$		2.7	1.0	3.0
1d	3,4,5-(OMe)$_3$	−0.03	4.3	0.99	4.8
1e	*p*-NMe$_2$	−0.83	0.094	1.00	0.1

[a] Measured by the photon-counting method. [b] Determined by the UV spectrum. [c] Calculated by $\Phi_{CL} = \Phi_r\Phi_S\Phi_F$ (Φ_F: fluorescence quantum yield of NMA, 0.9 in methanol).

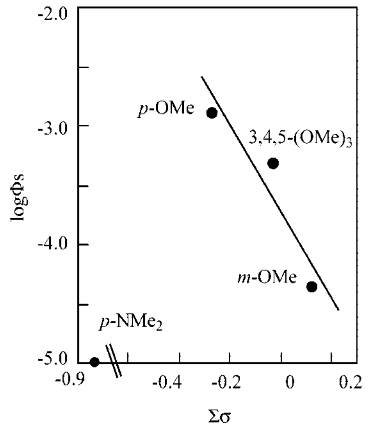


FIGURE 1. Hammett relationship of chemiluminescence singlet quantum yields.

To investigate such an effect of the dimethylamino group on the chemiluminescence inhibition, some spectral studies were carried out. Analysis of the reaction products from **1e** by ^{1}H

---

[6] (a) Chris, L.; Singer, L. A. *J. Am. Chem. Soc.* **1980**, *102*, 3823–3829. (b) Sakanishi, K.; Kato, Y.; Mizukoshi, E.; Shimizu, K. *Tetrahedron Lett.* **1994**, *35*, 4789–4792. (c) Sakanishi, K.; Nugroho, M. B.; Kato, Y.; Yamazaki, N. *Tetrahedron Lett.* **1994**, *35*, 3559–3562.

[7] Adam, W. In *The chemistry of peroxide*; Patai, S., Ed.; John Wiley & Sons: New York, 1983; pp 829–920.

[8] Perkizas, G.; Nikokavouras, J. *Monatsh. Chem.* **1983**, *114*, 3–11.

[9] Perkizas, G.; Nikokavouras, J. *Monatsh. Chem.* **1986**, *117*, 89–95.

[10] Foote, C.; Wexler, S.; Ando, W.; Higgins, R. *J. Am. Chem. Soc.* **1968**, *90*, 975–981.

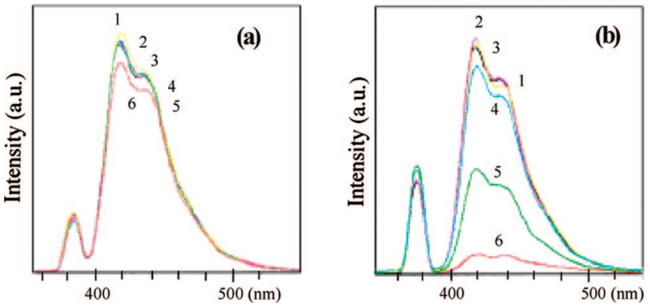


FIGURE 2. The change in the fluorescence spectral intensity with the addition of the quenchers: (a) 4-(dimethylamino)benzaldehyde as a quencher and (b) *N*,*N*-dimethylaniline as a quencher. The ratios of [quencher]/[NMA] are 0 shown by trace 1 (black), 0.1 bytrace 2 (pink), 1 by trace 3 (yellow), 10 by trace 4 (blue), 100 by trace 5 (green), and 1000 by trace 6 (red), respectively.

NMR revealed that two fragments, NMA and 4-(dimethylamino)benzaldehyde, were formed as a 1:1 mixture, which suggests that the singlet oxygenation proceeded to form the dioxetane intermediate even in this almost nonchemiluminescent reaction. Additionally, the oxidation of **1a** emits light even in the presence of a large excess amount of two amino compounds as quenchers, i.e., 4-(dimethylamino)benzaldehyde and *N*,*N*-dimethylaniline. Thus, the chemiluminescence inhibition due to deactivation of the singlet oxygen[11] is ruled out. On the other hand, only a slight change in the fluorescence intensity of NMA was observed when a large excess amount of 4-(dimethylamino)benzaldehyde was added to the NMA solution, but *N*,*N*-dimethylaniline showed a much stronger fluorescence quenching effect than the aldehyde (Figure 2). Thus, the fluorescence quenching effect of the dimethylamino group was established[12] and the effect is considered to arise from photoinduced electron transfer (PET) or the dissipation of the excitation energy of NMA due to rotation of the dimethylamino group if the fluorescence quenching is caused in a similar manner to the benzoxazinone derivative with dimethylamino group.[13a] Attachment of the formyl group electronically conjugating with the dimethylamino group in 4-(dimethylamino)benzaldehyde might reduce both the electron density of the nitrogen atom and the free rotation of the dimethylamino group, resulting in decreasing quenching ability. Although the fluorescence quenching by these quenchers is weak in the intermolecular system, it would be strong enough to quench the emitter, the excited NMA, if such an interaction would work in a solvent cage and even in an intermolecular fashion.

The remarkable effect of the amino group prompted us to apply it to the possibility of a molecular device, that is, the chemiluminescence could be controlled by the coexisting metal cations, if the quenching ability is modulated by metal chelation. Some fluorescent devices bearing the azacrowns as the ionophores are known to change their fluorescence spectra in the presence of suitable metal cations.[13] When the metal cation is incorporated in the cavity of the crown, the fluorescence maxima shift, in many cases, to the somewhat shorter wavelengths with a change in their intensities. Such a spectral change is the basis for application of the metal ion fluorescence sensing employing the crown compounds. Therefore, we prepared the benzylidenacridan (**2**) with 15-monoazacrown-5 as the metal ion recognition site and examined whether it acts as a chemiluminescent molecular device for a metal ion sensing system. Two benzylidenacridans **2** and **1e** as a control compound were reacted with singlet oxygen generated from a mixed solution of tetrabutylammonium hydroxide and aqueous hydrogen peroxide in acetonitrile,[14] which is one way to generate singlet oxygen without metal cations. As expected, only a slight light emission was observed for **2** and **1e**, in which the total chemiluminescence quantum yields (Φ_{CL}) were estimated to be 4.6×10^{-5} einstein/mol for **2** and 1.2×10^{-5} einstein/mol for **1e**. These chemiluminescence reactions can be regarded as almost nonchemiluminescent in a sense. The stronger chemiluminescence inhibition of the dimethylamino group compared to the azacrown seems to reflect the larger free rotation of the dimethylamino group than the azacrown.[13a] Upon the addition of the alkaline metal perchlorites, enhancement of the chemiluminescence efficiency with increasing metal ion concentration was detected, while no significant change was observed for **1e** even in the presence of a large excess amount of the metal cations. Among the alkaline metal cations, the sodium cation was the most effective, but the Φ_{CL} increased by only ca. 7 times compared to the case without the sodium cation. A much larger effect was observed when the divalent cations, magnesium or calcium ions, were added instead, and the Φ_{CL} values increased by almost 20 times compared to that without those cations. Unfortunately, the effect of barium ion at high concentration was not known because of insolubility of its perchlorite in this solvent system. A large excess amount of the cations is needed to obtain this emission intensity probably because of the decreased metal ion binding ability of the crown in the aqueous media. All the results are shown in Figure 3. Consequently, this azacrown compound was revealed to work as a tentative, chemiluminescent device providing information about coexisting metal cations.

To explore the chelation effect of **2**, a spectral study was carried out. Since the fluorescence intensity increased with the increasing calcium ion concentration as shown in Figure 4, **2** might be one of the fluorescence sensors that is also chemiluminescent. The gradual change in the fluorescence spectrum allowed us to estimate the stability constants assuming that 1:1 complexes are formed.[15] These values are presented in Table 2, and those for the divalent metal cations are greater than those for alkaline metals. As the cavity size of the 15-monoazacrown-5 is between 1.7 and 2.2 Å, sodium and calcium cations fit its cavity.[16] A slightly larger effect of the sodium cation among the alkaline metals and a much larger effect of the calcium ion agree with the adaptation, although the stability constants for the alkaline metals do not agree with this adaptation. It is suggested that the lithium cation is solvated with solvent molecules that gives the higher stability constants than expected for the ionic diameter of the free lithium cation.[17] The enhancement of calcium ion is the most satisfactory from the

---

(11) Darmanyan, A. P.; Jenks, W. S. *J. Phys. Chem. A* **1998**, *102*, 7420–7426.

(12) (a) Griesbeck, A. G.; Schieffer, S. *Photochem. Photobiol. Sci.* **2003**, *2*, 113–117. (b) Motoyoshiya, J.; Zhu, F.; Nishii, Y.; Aoyama, H. *Spectrochim. Acta, Part A* **2008**, *69*, 167–173.

(13) (a) Fery-Forgues, S.; Le Bris, M.-T.; Guette, J.-P.; Valeur, B. *J. Phys. Chem.* **1988**, *92*, 6233–6237. (b) Bourson, J.; Pouget, J.; Valeur, B. *J. Phys. Chem.* **1993**, *97*, 4552–4557. (c) Dumon, P.; Jonusauskas, G.; Dupuy, F.; Pee, P.; Rulliere, C.; Letard, J.- F.; Lapouyade, R. *J. Phys. Chem.* **1994**, *98*, 10391–10396. (d) Mathevet, R.; Jonusauskas, G.; Rulliere, C.; Letard, J.-F.; Lapouyade, R. *J. Phys. Chem.* **1995**, *99*, 15709–15713. (e) Crochet, P.; Malval, J.-P.; Lapouyade, R. *Chem. Commun.* **2000**, 289–290.

(14) (a) McKeown, E.; Waters, W. A. *Nature* **1964**, *203*, 1063. (b) Almeida, E. A.; Miyamoto, S.; Martinez, G. R.; Medeiros, M. H. G.; Mascio, P. D. *Anal. Chim. Acta* **2003**, *482*, 99–104.

(15) De Silva, A. P.; De Silva, S. A. *J. Chem Soc., Chem. Commun.* **1986**, 1709–1910.

(16) (a) Dietrich, B. *J. Chem. Educ.* **1985**, *62*, 954–964. (b) Pedersen, C. J.; Frendsdorf, H. K. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 16–25.

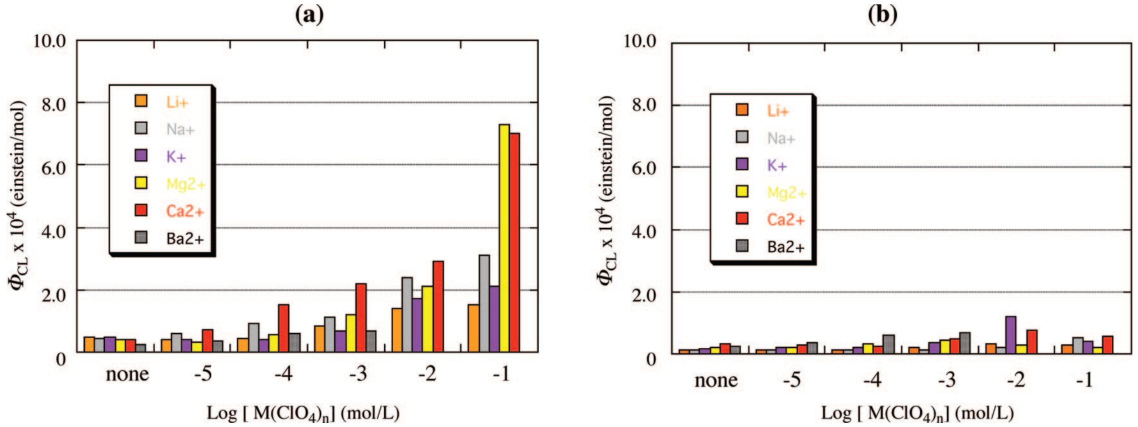


FIGURE 3. Metal cation effect on the chemiluminescence quantum yield (a) for azacrowned compound **2** and (b) for dimethylamino derivative **1e**. [**2**] = [**1e**] = 1 × 10^{-6} M.

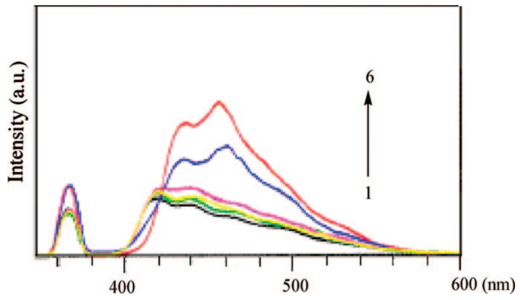


FIGURE 4. Fluorescence spectral change of **2** in the presence of calcium perchlorite in acetonitrile, [**2**] = 1.0 × 10^{-5} M: (1) no addition of Ca(ClO$_4$)$_2$, (2) [Ca(ClO$_4$)$_2$] = 1 × 10^{-5} M, (3) 1 × 10^{-4} M, (4) 1 × 10^{-3} M, (5) 1 × 10^{-2} M, (6) 1 × 10^{-1} M.

TABLE 2. **Stability Constants and Ionic Diameters**[a]

	Li^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	Ba^{2+}
ionic diameter (Å)	1.16	1.94	2.66	1.32	1.98	2.68
log *K*	1.98	1.17	2.03	3.01	2.71	3.3

[a] From ref 18.

viewpoints of both the ionic diameter and the stability constant. Considering the enhancement of the Φ_{CL} by magnesium ion as well as calcium ion, in spite of the absence of the data for barium ion, it might be probable that the divalent cations with the higher charge densities are more effective in binding to the azacrown than the monovalent cations.

Since the change in the fluorescence lifetime of the emitter is thought to be an important factor in the present system, the measurements were carried out under various conditions in the presence of the quencher and calcium ions (Table 3). The lifetime of the free NMA in acetonitrile is about 7.5 ns. Shortening of the fluorescence lifetime by about 1 ns was found after the addition of an equimolar amount of the azacrowned benzaldehyde, another fragment of the chemiluminescent reaction. On the other hand, when 1 equiv of calcium ion to the crown was added to the solution of both compounds, the lifetime was recovered to that of free NMA. A remarkable prolongation of the lifetime was observed at the higher concentration. It is noteworthy that when a 10^4 times larger excess amount of calcium ion compared to the azacrown benzaldehyde is added, there are two fluorescent species with the lifetimes of 9.52 and 18.28 ns, the latter of which is almost 2.7 times longer than the case without the calcium ion. Although we cannot identify what kind of complexes are formed between the azacrown and calcium ions for such a prolongation of the lifetime, the interaction obviously prevents the dissipation of the energy of the excited emitter. At present this is one of the explanations why the incorporation of metal cations to the crown enhances the chemiluminescence.

TABLE 3. **The Change in the Fluorescence Lifetime (*τ*) of NMA**[a]

aldehyde (M)	Ca(ClO$_4$)$_2$ (M)	order	lifetime *t* (ns)
none	none	1	7.607
10^{-6}	none	1	6.716
	10^{-6}	1	7.489
	10^{-5}	1	7.607
	10^{-4}	1	7.607
	10^{-3}	1	9.118
	10^{-2}	2	9.522 (51%), 18.279 (49%)

[a] [NMA] = 10^{-6} M in acetonitrile.

In conclusion, we applied the chemiluminescence inhibition of the amino-substituted benzylidenacridans to a metal ion recognizing system using the azacrowned compound that modulates the chemiluminescence in the presence of suitable metal ions such as magnesium and calcium ions. While there are some points to be improved, for instance, the quenching system with the interaction by an intramolecular manner would be much better, we present a chemiluminescent reaction that is potentially interesting for developing a molecular device for metal ion sensing. Well-refined chemiluminescent molecules can be developed for sensing various important target molecules and this is currently underway in our laboratory.

Experimental Section

General methods are provided as Supporting Information.

9-(4′-Methoxybenzylidene)-1-methyacridan (1a). To a solution of 9-diethylphosphono-10-methylacridan (1.0 g, 3.02 mmol) in tetrahydrofuran (THF) (10 mL) was added a solution of *t*-BuOK (0.51 g, 4.53 mmol) in THF (5 mL) and a solution of *p*-methoxybenzaldehyde (0.36 mL, 3.02 mmol) in sequence. After the mixture was stirred for 8 h at room temperature, the solvent was removed under reduced pressure. The residue was dissolved in ethyl acetate and washed with saturated ammonium chloride solution and brine. After the organic layer was dried over anhydrous Na$_2$SO$_4$ and the solvent was removed under reduced pressure, the

---

(17) Pacey, G. E.; Wu, Y. P. *Talanta* **1984**, *31*, 165–168.
(18) *Handbook of Chemistry and Physics*, 66th ed.; CRC Press: Boca Ratan, FL, 1995.

crude product was purified by column chromatography on silica gel with ethyl acetate and hexane as the eluants to give a yellow crystal (0.26 g, 28%). Mp 143 °C. ^{1}H NMR δ 3.48 (s, 3H), 3.80 (s, 3H), 6.62 (s, 1H), 6.72−7.69 (m, 12H). ^{13}C NMR δ 33.9, 55.6, 106.9, 112.7, 113.5, 114.0, 120.3,121.6, 122.9, 123.8, 128.1, 128.6, 129.0, 134.1. MS (*m/z*) 313 (M$^+$). Anal. Calcd for $C_{22}H_{19}NO$: C, 84.31; H, 6.11; N, 4.47. Found: C, 84.35; H, 6.20; N, 4.45.

9-(3′-Methoxybenzylidene)-1-methyacridan (1b). A similar procedure to the above with phosphonoacridan (0.51 g, 1.51 mmol), *t*-BuOK (0.25 g, 2.26 mmol), and *m*-methoxybenzaldehyde (0.18 mL, 1.51 mmol) gave a viscous oil (0.26 g, 28%), which was unstable and decomposed gradually. ^{1}H NMR δ 3.48 (s, 3H), 3.67 (s, 3H), 6.63 (s, 1H), 6.69−7.71 (m, 12H). ^{13}C NMR δ 33.9, 56.5, 112.8, 113.0, 113.6, 113.8, 120.3,121.7, 121.7, 122.9, 124.0, 128.4, 129.0, 129.4, 129.6. MS (*m/z*) 313 (M$^+$).

9-(2′,4′-Dimethoxybenzylidene)-10-methylacridan (1c). A similar procedure to the above with phosphonoacridan (0.51 g, 1.51 mmol), *t*-BuOK (0.51 g, 4.53 mmol), and 2,4-dimethoxybenzaldehyde (0.25 g, 1.51 mmol) gave a yellow crystal, which was recrystallized from benzene (0.24 g, 46%). Mp 142 °C. ^{1}H NMR δ 3.43 (s, 3H), 3.76 (s, 3H), 3.80 (s, 3H) 6.29 (m, 1H), 6.45−7.76 (m, 12H). ^{13}C NMR δ 33.4, 55.4, 55.9, 98.8, 104.8, 112.6, 113.3, 118.7, 120.3, 121.5, 124.1, 128.0, 128.3, 128.9, 130.1. MS (*m/z*) 343 (M$^+$). Anal.Calcd for $C_{23}H_{21}NO_2$: C, 80.44; H, 6.16; N, 4.08. Found: C, 80.80; H, 6.29; N, 4.11.

9-(3′,4′,5′-Trimethoxybenzylidene)-10-methylacridan (1d). A similar procedure to the above with phosphonoacridan (0.51 g, 1.51 mmol), *t*-BuOK (0.51 g, 4.53 mmol), and 3,4,5-trimethoxybenzaldehyde (0.30 g, 1.51 mmol) gave a yellow crystal (0.09 g, 16%). Mp 137 °C. ^{1}H NMR δ 3.50 (s, 3H), 3.71 (s, 6H), 3.85 (s, 3H), 6.57−7.71 (m, 11H). ^{13}C NMR δ 33.9, 56.1, 61.3, 106.1, 112.8, 113.6, 120.2, 121.7, 122.9, 123.8, 128.3, 128.9, 129.5, 134.0, 153.3. MS (*m/z*) 373 (M$^+$). Anal. Calcd for $C_{24}H_{23}NO_3$: C, 77.19; H, 6.21; N, 3.75. Found: C, 77.09; H, 6.30; N, 3.73.

9-(4′-Dimethylaminobenzylidene)-10-methylacridan (1e). A similar procedure to the above with phosphonoacridan (0.51 g, 1.51 mmol), *t*-BuOK (0.51 g, 4.53 mmol), and 4-(dimethylamino)benzaldehyde (0.23 g, 1.51 mmol) gave a yellow crystal (0.18 g, 38%). Mp 116 °C. ^{1}H NMR δ 2.93 (s, 3H), 3.42 (s, 3H), 6.59 (s, 1H), 6.61−7.68 (m, 12H). ^{13}C NMR δ 33.9, 40.9, 112.6, 112.7, 113.6, 120.4, 121.7, 123.7,124.0, 127.9, 128.5, 129.1, 130.0. MS (*m/z*) 326 (M$^+$). Anal.Calcd for $C_{23}H_{22}N_2$: C, 84.63; H, 6.79; N, 8.58. Found: C, 84.75; H, 6.87; N, 8.38.

9-[4′-(13″-Aza-1″,4″,7″,10″-tetraoxacyclopentadecan-13″-yl)benzylidene]-10-methylacridan (2). A similare procedure to the above with phosphonoacridan (0.72 g, 2.16 mmol), *t*-BuOK (0.49 g, 4.32 mmol), and 4-(13′-aza-1′,4′,7′,10′-tetraoxacyclopentadecan-13″-yl)benzaldehyde (0.35 g, 1.08 mmol) gave a yellow crystal (0.54 g, 93%). Mp 69 °C. ^{1}H NMR δ 3.47 (s, 3H), 3.56−3.77 (m, 20H), 6.59 (s, 1H), 6.57−7.63 (m, 12H). ^{13}C NMR δ 33.8, 52.9, 69.1, 70.5, 70.6, 71.7, 111.4, 112.5, 113.5, 120.3, 121.6, 121.7, 123.6, 123.9, 125.8, 127.7, 128.2, 128.3, 128.9, 130.0, 134.2, 142.0, 143.8,146.6. MS (*m/z*) 500 (M$^+$). HRMS calcd for $C_{31}H_{36}O_4N_2$ 500.2647, found 500.2645.

Chemiluminescence Quantum Yields (Φ_{CL}). The measurements were carried out by a photon-counting method with a Hamamatsu Photonics R464 photomultiplier connected to a photon-counting unit (C3866) and a photon-counting board M8784 according to a previously reported procedure,[19] and the luminal chemiluminescence was used as the standard in DMSO for calibration of the photomultiplier tube. For a typical run, an aqueous solution of hydrogen peroxide (1.0×10^{-5} M) (0.5 mL) and an aqueous solution of tetrabutylammonium hydroxide (1.0×10^{-2} M) were added to a solution of **2** in acetonitrile (MeCN) (1.0×10^{-6} M) (1 mL) in a quartz cell placed in front of the photomultiplier at 25 °C and the photons generated for a 5 min period were counted. The average of the values obtained by a few measurements was used for the calculation of Φ_{CL}. For the measurement in the presence of the metal salt, a solution containing a certain concentration of metal perchlorites in MeCN was added to the solution of **2** in MeCN and left to stand for 2 h before being mixed with the solution of alkaline hydrogen peroxide.

Acknowledgement. One of the authors (J.M.) is thankful for the financial support by a Grant-in-Aid (19550137 and the Grobal COE program), from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

Note Added after ASAP Publication. Reference 19 was added in the version published on January 13, 2009.

Supporting Information Available: General method for the Experimental Section, the typical fluorescence decays of NMA, ^{1}H NMR spectra of **1c**, **1d**, and **2**, and ^{13}C NMR spectrum of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO801556P

---

[19] (a) Motoyoshiya, J.; Sakai, N.; Imai, M.; Yamaguchi, Y.; Koike, R.; Takaguchi, Y.; Aoyama, H. *J. Org. Chem.* **2002**, *67*, 7314–7318. (b) Motoyoshiya, J.; Ikeda, T.; Tsuboi, S.; Kusaura, T.; Takeuchi, Y.; Hayashi, S.; Yoshioka, S.; Takaguchi, Y.; Aoyama, H. *J. Org. Chem.* **2003**, *68*, 5950–5955.