

Performance of Tris(2-methyl-8-quinolinolato)aluminum as Fluorescent Anionophore

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An X-ray crystallographic study demonstrated that the tris complex of Al^{3+} with 2-methyl-8-quinolinol (Hmq), $[\text{Al}(\text{mq})_3]$, had a discrete octahedral geometry in a meridional configuration with respect to mq[−]; the Al-N bonds were appreciably elongated. In organic solvents, the complex reacted with water to give a lower species of a μ -oxo dimer, $[\text{Al}_2\text{O}(\text{mq})_4]$, and a protonated ligand, depending on the concentrations of water and of excess ligand. None of Cl^- , Br^- , I^- , ClO_4^- , and CH_3COO^- showed any reactions with $[\text{Al}(\text{mq})_3]$. The anions having high affinities to Al^{3+} , such as H_2PO_4^- and F^- , replaced all the ligand. The anion having a lower affinity, HSO_4^- , exclusively formed a mixed-ligand complex of $[\text{Al}(\text{mq})_2\text{HSO}_4]$, which had a more intense fluorescence than the others. In contrast, the corresponding 8-quinolinol (Hq) complex, $[\text{Alq}_3]$, showed no reactions with any anions.

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Introduction

Sensing ions and molecules by fluorescent chemosensors is highly applicable to a wide range of technologies and has currently been studied intensively.^{1,2} Lewis acid-base reactions are extensively used as a driving force for the recognition of cations, while hydrogen-bondings are mainly used for the recognition of anions. One application of the Lewis acid-base reactions to anion-sensing is the fluorometric detection of fluoride with boron-containing compounds.^{3,4} The high affinity of boron to fluoride and the change in fluorescent characteristics with an increase in coordination number of boron were successfully utilized for the detection of fluoride.

The group 13 metal complexes with 8-quinolinol derivatives (Hq: 8-quinolinol, Hmq: 2-methyl-8-quinolinol) have recently been attracting much attention as a component of the organic light-emitting device. The aluminum complex with a parent compound of 8-quinolinol, $[\text{Alq}_3]$, has been used as a green light-emitting material.⁵ The effects of substituents on the optical performance were studied; $[\text{Al}(\text{mq})_3]$ was reported to show a blue emission, which was ascribed to an electron-donating methyl group.⁶ Later, the mixed-ligand complex with Hmq and phenol (PhOH), $[\text{Al}(\text{mq})_2(\text{OPh})]$, has been proposed as an alternative having a higher chemical stability.^{7,8}

To explore the further possibility of the Lewis acid-base reactions for the fluorometric detection of anions, we have studied the reactions of these aluminum complexes ($[\text{Al}(\text{mq})_3]$, $[\text{Al}_2\text{O}(\text{mq})_4]$, and $[\text{Alq}_3]$) with anions (F^- , Cl^- , Br^- , I^- , ClO_4^- , HSO_4^- , H_2PO_4^- , and CH_3COO^-) in nonaqueous solvents and have found a unique reactivity of $[\text{Al}(\text{mq})_3]$.

Experimental

Preparation

The complex $[\text{Al}(\text{mq})_3]$ was prepared by the reaction of aluminum isopropoxide (5 mmol) with Hmq (15 mmol) in dehydrated EtOH (Found: Al, 4.93; EtOH (a weight-loss by heating at 80°C), 8.37%. Calcd for $\text{AlC}_{30}\text{H}_{24}\text{N}_3\text{O}_3 \cdot \text{EtOH}$: Al, 4.93, EtOH, 8.41%. Yield 73%). The lower complex, $[\text{Al}_2\text{O}(\text{mq})_4]$, was similarly prepared at a molar ratio of 1:2 in EtOH containing water and recrystallized from dimethyl sulfoxide (Found: Al, 7.64%, Calcd for $\text{Al}_2\text{C}_{40}\text{H}_{32}\text{N}_4\text{O}_5$: Al, 7.67%. Yield 28%. IR(Al-O-Al) 1017 cm^{-1}). The complex $[\text{Alq}_3]$ was prepared by the conventional precipitation method from aqueous solutions.

Spectroscopic studies

The solvents were dehydrated with molecular sieves; the residual water concentrations were 10^{-2} mol dm^{-3} for DMSO and DMF and 5×10^{-2} mol dm^{-3} for EtOH. The tetrabutylammonium (Q^+) salts of F^- , Cl^- , Br^- , I^- , ClO_4^- , HSO_4^- , H_2PO_4^- , and CH_3COO^- were used to examine the reactions of metal complexes with these anions. A series of solutions containing metal complexes (10^{-5} mol dm^{-3} for $[\text{Al}_2\text{O}(\text{mq})_4]$ and 10^{-4} mol dm^{-3} for the others) and anions up to a molar ratio of 9 against Al were prepared, and their spectroscopic properties were evaluated. In the presence of an excess Hmq, the absorbance at 400 nm and the fluorescence at 510 nm with an excitation at 400 nm were monitored to avoid the absorption by Hmq. In the absence of any excess Hmq, the absorbance at 310 and 360 nm and the fluorescence at 480 nm with an excitation at 360 nm were also monitored. The lifetime of photoluminescence was measured with a time-resolved spectroscopic system, PTI-5100S (Photon Technology International).

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Table 1 Crystallographic data and experimental details for $[\text{Al}(\text{mq})_3](\text{CH}_3\text{CH}_2\text{OH})$

Formula	$\text{AlC}_{32}\text{H}_{30}\text{N}_3\text{O}_4$	$F(0\ 0\ 0)$	2304.00
Formula weight	547.59	μ	$1.15\ \text{cm}^{-1}$
Crystal system	orthorhombic	$2\theta_{\text{max}}$	51.4°
Space group	$Pbca$	No. of Reflections observed	17734
Lattice parameters	$a = 17.001(3)\text{\AA}$ $b = 20.266(5)\text{\AA}$ $c = 16.243(1)\text{\AA}$ $V = 5596(1)\text{\AA}^3$	No. of Reflections used ($I > 2\sigma(I)$)	8191
		No. of Variables	421
		R_1^a	0.071
		R_w^b	0.189
Z	8	Largest residuals	$0.54, -0.49\ \text{e}\text{\AA}^{-3}$
ρ	$1.300\ \text{g cm}^{-3}$	Shift/Error	0.202

a. $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for $I > 2\sigma(I)$ data. b. $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w^{-1} = \sigma^2(F_o^2)$.

X-ray crystal structure analysis

The crystallographic data for $[\text{Al}(\text{mq})_3]\cdot\text{EtOH}$ are summarized in Table 1. A yellow needle-like single crystal was sealed in a glass capillary, and the X-ray diffraction data were collected at 283 K on a Rigaku R-Axis-IV imaging plate area detector with graphite-monochromated Mo K_α radiation ($\lambda = 0.71073\ \text{\AA}$). Among these data, 25 reflections with $2\theta = 20 - 25^\circ$ were also collected on an Enraf Nonius CAD4 four-circle automated diffractometer under the same conditions. The accurate unit-cell parameters used for the refinement were determined by least-squares calculation of the setting angles of these reflections. All the reflection data were corrected for Lorentz and polarization effects, and the independent reflections with $I_o \geq 2\sigma(I_o)$ were used for structure analysis calculation.

The structure was solved by the direct method (SAPI 91)⁹ and was refined anisotropically for non-hydrogen atoms by the full-matrix least-squares technique. Refinement was continued until all shifts became smaller than one third of the standard deviations of the parameters. The solvated ethanol molecules were disordered; the occupancy factors of O atoms of ethanol, O(2) and O(3), were respectively converged to 0.7 and 0.3 by isotropic treatment. Atomic scattering factors and anomalous dispersion terms were taken from the literature.¹⁰ All hydrogen atoms other than H atoms of methyl groups and of disordered ethanol molecules were located in the difference Fourier map and were treated isotropically. H(7A), H(8A), H(6B), H(7B), H(8B), H(6C), H(7C), H(8C), and H(4B) were located at the positions calculated with C-H = $0.95\ \text{\AA}$ and their thermal parameters were related to those of their parent atoms according to $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The minimized function was $\Sigma w(F_o^2 - F_c^2)^2$ with the weighting scheme, $w = (\sigma^2(F_o))^{-1}$. The final R_1 value was 0.071 for 8191 reflections with $I > 2\sigma(I)$, and the final R_w value was 0.189 for all reflections (425 parameters). The max shift/error in the final cycle was 0.202, and the final difference Fourier map did not show any significant peaks, except for the environment of the Al atom. All the calculations were performed on an IRIS-Indigo computer by using the teXsan crystallographic software package.¹¹

Results and Discussion

Preparation and crystal structure of $[\text{Al}(\text{mq})_3]$

2-Methyl-8-quinolinol had been proposed as one of the 8-quinolinol derivatives with a specificity of not precipitating aluminum from an aqueous solution. In the 1960s, however, some evidence for 1:2 species was found in absolute EtOH and in the solvent extraction system,^{12,13} and some for the tris complex in a molten Hmq system.¹⁴ Later, selective preparation of these complexes was established using different organic

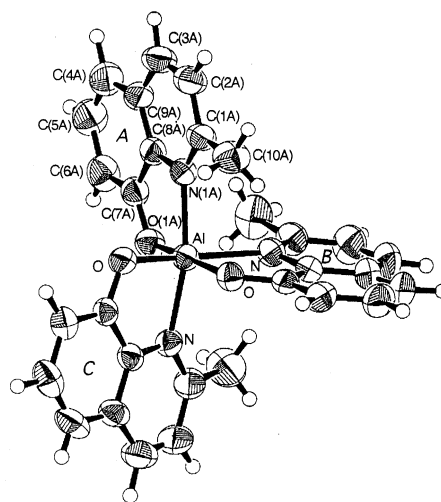


Fig. 1 Molecular structure of $[\text{Al}(\text{mq})_3]$. Al-O(1A) = $1.821(1)$, Al-O(1B) = $1.816(1)$, Al-O(1C) = $1.853(1)$, Al-N(1A) = $2.083(1)$, Al-N(1B) = $2.255(1)$, Al-N(1C) = $2.109(1)\text{\AA}$.

solvents like chloroform and DMSO.¹⁵ The methods of precipitating the tris complex from aqueous media were also developed by the use of an auxiliary ligand including OH^- .^{16,17} The lower species was determined to be a μ -oxo dimer, $[\text{Al}_2\text{O}(\text{mq})_4]$, by X-ray crystallography,¹⁸ although a contradictory assignment is still pending.¹⁹ On the other hand, the structure of the tris complex has not been studied. Recently, the structure of $[\text{Al}(\text{mq})_2\text{q}]$, which was obtained by the reaction of $[\text{Al}(\text{Et})(\text{mq})_2]$ with Hq, was reported, but it was described that the corresponding reaction with Hmq only gave the starting material.²⁰

The tris complex was prepared by using aluminum isopropoxide and an ethanol medium, and was isolated as an ethanol solvate. Figure 1 shows the molecular structure of $[\text{Al}(\text{mq})_3]$, which has a discrete octahedral geometry in a meridional configuration with respect to mq^- . Compared with $[\text{Alq}_3]$ and $[\text{Al}(\text{mq})_2\text{q}]$ having the corresponding structures,^{20,21} Al-O (av. $1.83\ \text{\AA}$) is shortened by 0.02 and 0.01 \AA , and Al-N (av. $2.15\ \text{\AA}$) is elongated by 0.10 and 0.05 \AA , respectively. A similar trend, due to the repulsion between Me groups and neighboring atoms, was observed in the tris complexes of nickel(II).^{22,23} The distances between a Me group of one mq^- and a coordinating atom of another mq^- (C(10A)···O(1B): $3.034(3)$; C(10B)···O(1A): $3.038(3)$; C(10C)···N(1B): $3.215\ \text{\AA}$) were still shorter than those of nickel(II) complexes. Since such repulsion is reduced in the lower species of $[\text{Al}_2\text{O}(\text{mq})_4]$, Al-N

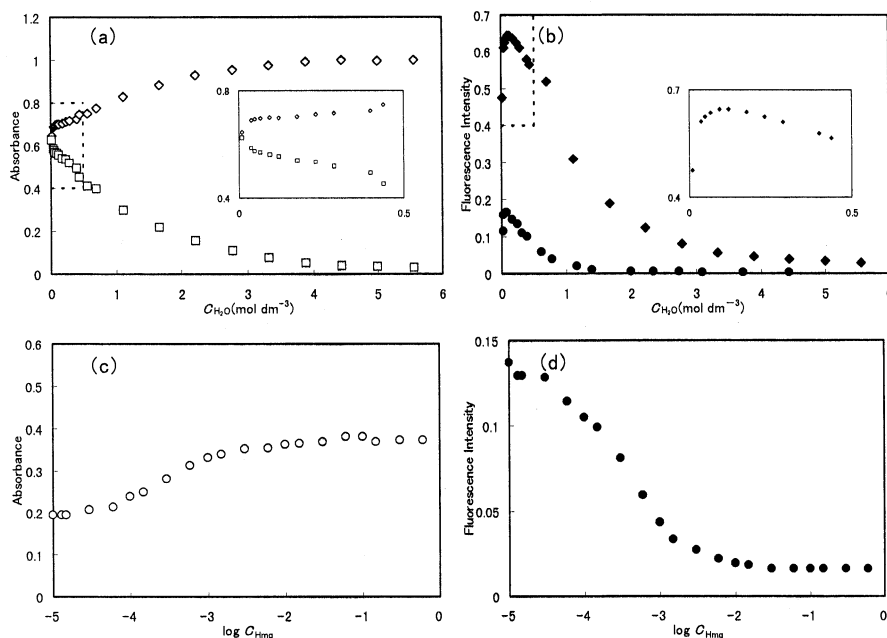


Fig. 2 Effects of water (a, b) and excess Hmq (c, d) concentrations on the absorbance (a, c) and fluorescence (b, d) of $[\text{Al}(\text{mq})_3]$ in DMSO. (a, c) wavelength/nm: (\diamond) 310, (\square) 360, (\circ), 400. (b, d) λ_{ex} , λ_{em} /nm: (\blacklozenge) 360, 480, (\bullet) 400, 510. $C_{\text{Al}} = 10^{-4} \text{ mol dm}^{-3}$.

(av.) is shortened by 0.06 \AA with a slight reduction in Al–O (av.).¹⁸

In agreement with the conclusions of the synthetic studies in late 1960s,^{12–17} $[\text{Al}(\text{mq})_3]$ does exist in solid states, but the weakened Al–N bonds suggest the instability of this complex.

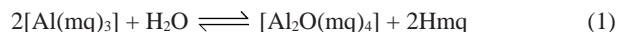
Dissolution states of $[\text{Al}(\text{mq})_3]$ in organic solvents

The absorption spectra of $[\text{Al}(\text{mq})_3]$ dissolved in DMSO, DMF, and EtOH were recorded. They were appreciably different from one another; the absorbance at 360 nm, which is characteristic of free or coordinated mq^- , decreased, while the absorbance at 310 nm, which is characteristic of Hmq, increased in the order of DMSO, DMF, EtOH. This order agrees well with that of the residual water concentration. DMSO was accordingly selected for the subsequent studies.

When water was added to the DMSO solution of $[\text{Al}(\text{mq})_3]$, the absorbance at 360 nm (\square) decreased and became negligible at 5 mol dm^{-3} (Fig. 2a). The absorbance at 310 nm (\diamond), on the other hand, increased with plateaus at two water concentrations of around 10^{-1} and $>5 \text{ mol dm}^{-3}$. The fluorescence maximum, with an excitation at 400 nm, was shifted from 488 to 480 nm. The fluorescence intensities (\blacklozenge : $\lambda_{\text{ex}} = 360 \text{ nm}$, $\lambda_{\text{em}} = 480 \text{ nm}$; \bullet : $\lambda_{\text{ex}} = 400 \text{ nm}$, $\lambda_{\text{em}} = 510 \text{ nm}$) showed convex profiles respectively having a maximum at $10^{-1} \text{ mol dm}^{-3}$ (Fig. 2b). The emission intensity at this concentration almost agreed with that of $[\text{Al}_2\text{O}(\text{mq})_4]$ directly dissolved in DMSO.

When an excess Hmq was added to the DMSO solution of $[\text{Al}(\text{mq})_3]$ at a constant water concentration of around $10^{-2} \text{ mol dm}^{-3}$, the absorbance at 400 nm (\circ), where Hmq has negligible absorption, increased and became constant at a concentration $>10^{-2} \text{ mol dm}^{-3}$ (Fig. 2c). The fluorescence maximum was shifted from 488 to 513 nm, and the fluorescence intensity (\bullet) decreased and became constant at a concentration $>10^{-2} \text{ mol dm}^{-3}$ (Fig. 2d).

All these findings are explained by the following reactions:



When $[\text{Al}(\text{mq})_3]$ was dissolved in organic solvents not containing any excess Hmq, the reaction with water given by Eq. (1) yielded the lower species of $[\text{Al}_2\text{O}(\text{mq})_4]$ as well as Hmq; a molar fraction of Al in the form of $[\text{Al}_2\text{O}(\text{mq})_4]$ was 60–70% in DMSO containing $10^{-2} \text{ mol dm}^{-3}$ water. The addition of water at a concentration of $10^{-1} \text{ mol dm}^{-3}$ completed the conversion to $[\text{Al}_2\text{O}(\text{mq})_4]$, but a further addition induced an extended dissociation of the ligands by Eq. (2). On the other hand, the addition of Hmq up to $10^{-2} \text{ mol dm}^{-3}$ guaranteed the quantitative formation of $[\text{Al}(\text{mq})_3]$.

Such dissociation reactions were not observed for $[\text{Alq}_3]$, but have been reported and quantitatively explained for $[\text{V}_2\text{O}_3\text{q}_4]$ in chlorobenzene.²⁴ The water in aprotic solvents is appreciably acidic and easily replaces the weakly bound ligand to give a lower species and a protonated ligand.

Reactions of complexes with anions

The reactions of $[\text{Al}(\text{mq})_3]$, $[\text{Al}_2\text{O}(\text{mq})_4]$ and $[\text{Alq}_3]$ with a series of anions in the absence of an excess ligand were monitored by both UV and fluorescence spectroscopy. Only H_2PO_4^- , F^- , and HSO_4^- caused appreciable changes on the spectrum of $[\text{Al}(\text{mq})_3]$, and only H_2PO_4^- and F^- on the spectrum of $[\text{Al}_2\text{O}(\text{mq})_4]$, while no changes were found for Cl^- , Br^- , I^- , ClO_4^- , or CH_3COO^- . In contrast, none of these anions caused any change on the spectrum of $[\text{Alq}_3]$. In agreement with the tendency to react with water, $[\text{Alq}_3]$ is much more stable than $[\text{Al}(\text{mq})_3]$ and $[\text{Al}_2\text{O}(\text{mq})_4]$.

The reaction of $[\text{Al}(\text{mq})_3]$ with QH_2PO_4 decreased the absorbance at 360 nm and increased the absorbance at 310 nm (\square and \diamond in Fig. 3a, respectively). This indicated the dissociation of mq^- to form Hmq. The fluorescence was quenched with a shift of the emission maximum to a longer

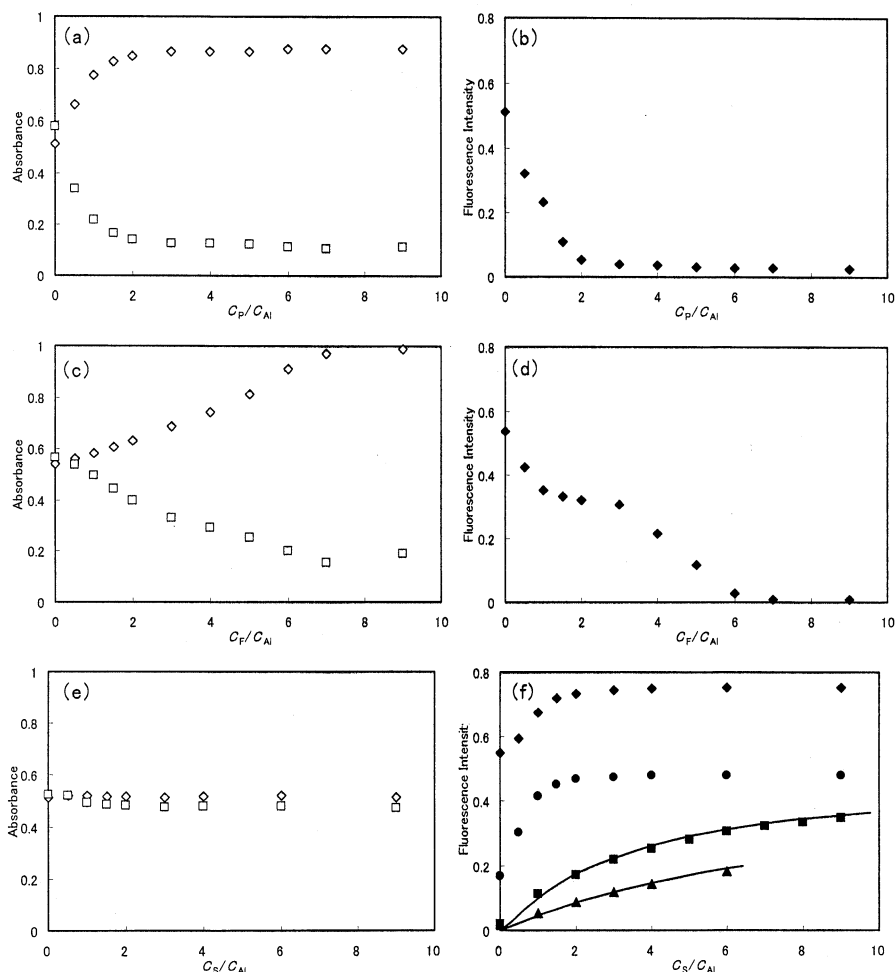


Fig. 3 Effects of $H_2PO_4^-$ (a, b), F^- (c, d), and HSO_4^- (e, f) on the absorbance (a, c, e) and fluorescence intensity (b, d, f) of $[Al(mq)_3]$. (a, c, e) wavelength/nm: (\diamond) 310, (\square) 360. (b, d, f) λ_{ex} /nm, λ_{em} /nm: (\diamond) 360, 480, (\bullet , \blacksquare , \blacktriangle) 400, 510. $C_{Hmq}/mol\ dm^{-3}$: (\diamond , \square , \blacklozenge , \bullet) 0; (\blacksquare) 0.01; (\blacktriangle) 0.03. The parameters on the abscissa, C_P , C_F , and C_S , indicate the total concentrations of phosphate, fluoride, and sulfate, respectively. The solid curves were obtained using the conditional equilibrium constants in the text.

wavelength (Fig. 3b). The molar ratio plot indicated the stoichiometry of 1:1. Thus, the reaction is expressed by Eq. (3) with the contribution of Eq. (1):

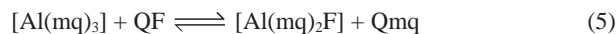


The red-shift of the emission spectra suggested that Eq. (1) was shifted to the left due to Hmq formed through the reaction given by Eq. (3). The absorption spectra at $C_P/C_{Al} = 2$ suggested that the resulting Qmq was also converted to Hmq by some reaction. The reaction of $[Al_2O(mq)_4]$ with QH_2PO_4 is practically the same as that of $[Al(mq)_3]$ and is expressed by Eq. (4):



The reaction of $[Al(mq)_3]$ with QF proceeded in two steps. The addition of QF up to $C_F/C_{Al} = 1$ only slightly changed the absorbance at both 310 nm and 360 nm (Fig. 3c). At a higher ratio, the changes were similar to those by the reaction with QH_2PO_4 . The fluorescence intensity with a plateau at $C_F/C_{Al} = 1$ (Fig. 3d) more clearly indicated the presence of an intermediate species. The fluorescence maximum was also red-shifted, due to the contribution of Eq. (1). Thus, the first reaction is

expressed by Eq. (5):



Such mixed-ligand complexes with a coordination number of five have been described to be stable in general.^{7,8} The second reaction formed AlF_3 as well as Hmq, which was also converted from Qmq by some reaction. The reaction of $[Al_2O(mq)_4]$ with QF caused only a small variation on the first reaction because of a minor change in coordination sphere, while the spectral change caused by the second reaction was the same as that by the second reaction of $[Al(mq)_3]$ with QF.

The reaction of $[Al(mq)_3]$ with $QHSO_4$ showed a different pattern from the others. The absorbance at both 310 nm and 360 nm only slightly changed up to $C_S/C_{Al} = 9$ (Fig. 3e). The fluorescence intensities (Fig. 3f, \blacklozenge : $\lambda_{ex} = 360$ nm, $\lambda_{em} = 480$ nm; \bullet : $\lambda_{ex} = 400$ nm, $\lambda_{em} = 510$ nm), on the other hand, were appreciably enhanced with a red-shift in the emission maximum. The molar ratio plots indicated the reaction stoichiometry of 1:1. An excess $QHSO_4$ caused no change. Thus, the reaction is expressed by Eq. (6) with the contribution of Eq. (1):

Table 2 Spectroscopic properties of Al-mq complexes^a

Complex	$\lambda_{\text{em}}/\text{nm}$	Relative F. I.	τ/ns
[Al(mq) ₂ (HSO ₄)]	500	0.51	22
[Al ₂ O(mq) ₄]	485	0.22	18
[Al(mq) ₃]	513	0.02	15

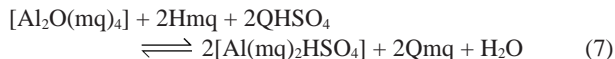
a. $\lambda_{\text{ex}} = 400 \text{ nm}$.



This specific reaction occurs even in the presence of 0.7 mol dm⁻³ water.

In the presence of an excess Hmq ($C_{\text{Hmq}}/\text{mol dm}^{-3}$: 0.01 for ■; 0.03 for ▲), the contribution of Eq. (1) was excluded, and the change in fluorescence was purely ascribed to Eq. (6). The equilibrium analysis based on the fluorescence intensity change gave the conditional equilibrium constants: $K' = [\text{Al}(\text{mq})_2\text{HSO}_4]/[\text{Al}(\text{mq})_3][\text{QH}\text{SO}_4]$: $10^{3.52}$ for $C_{\text{Hmq}} = 0.01 \text{ mol dm}^{-3}$, and $10^{3.07}$ for $C_{\text{Hmq}} = 0.03 \text{ mol dm}^{-3}$. The curves calculated using these constants reproduced the experimental points, respectively. The increase in conditional constant ($10^{0.45}$) by the decrease in log C_{Hmq} ($10^{-0.48}$) supports the conclusion that one ligand is dissociated on the reaction as given by Eq. (6); Qmq and Hmq are expected to be in equilibrium with each other in DMSO.

In contrast, [Al₂O(mq)₄] did not react with QH₂SO₄, but did react in the presence of Hmq. Thus, a free Hmq was essential for accommodation of the oxide ion bridging aluminum ions.



Spectroscopic properties

The spectroscopic characteristics of the complexes are summarized in Table 2. The fluorescence maximum of [Al₂O(mq)₄] were located at around 480 nm, which were similar to those of [Al(mq)₂(OPh)] ($\lambda_{\text{em}} = 470 - 486 \text{ nm}$).^{7,8} In contrast, the maximum of [Al(mq)₃] was located at a longer wavelength of 513 nm, which was similar to those of the other tris complexes with 8-quinolinol derivatives. The fluorescence intensities of [Al₂O(mq)₄] and [Al(mq)₂(HSO₄)] were much higher than that of [Al(mq)₃]. All these species showed practically the same lifetime.

Acknowledgements

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References

1. "Fluorescent Chemosensors for Ion and Molecule Recognition", ed. A. W. Czarnik, **1993**, ACS Symposium Series, 538.
2. A. P. De Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher, and T. E. Rice, *Chem. Rev.*, **1997**, 97, 1515.
3. C. R. Cooper, N. Spencer, and T. D. James, *J. Chem. Soc., Chem. Commun.*, **1998**, 1365.
4. A. Yuchi, J. Sakurai, A. Tatebe, H. Hattori, and H. Wada, *Anal. Chim. Acta*, **1999**, 387, 189.
5. C. H. Chen and J. Shi, *Coord. Chem. Rev.*, **1998**, 171, 161.
6. M. Matsumura and T. Akai, *Jpn. J. Appl. Phys.*, **1996**, 35, 5357.
7. Z. Shen, P. E. Burrows, V. Bulovic, S. R. Forrest, and M. E. Thompson, *Science*, **1997**, 276, 2009.
8. Y. Qiu, Y. Shao, D. Zhang, and Z. Hong, *Jpn. J. Appl. Phys.*, **2000**, 39, 1151.
9. SAPI91, H.-F. Fan, Structure Analysis Programs with Intelligent Control, Rigaku Corporation, **1991**, Tokyo, Japan.
10. J. A. Ibers and W. C. Hamilton (ed.), "International Tables for X-ray Crystallography", **1974**, Vol. IV, Kynoch, Birmingham.
11. teXsan, Crystal Structure Analysis Package, Molecular Structure Corporation, **1985** and **1992**.
12. W. E. Ohnesorge and A. L. Burlingame, *Anal. Chem.*, **1962**, 34, 1086.
13. Yu. A. Zolotov, L. A. Demina, and O. M. Petrukhin, *Zh. Anal. Khim.*, **1970**, 25, 1487.
14. G. R. Horton, *Anal. Chem.*, **1967**, 39, 1036.
15. P. R. Scherer and Q. Fernando, *Anal. Chem.*, **1968**, 40, 1938.
16. T. J. Cardwell, *Inorg. Nucl. Chem. Lett.*, **1969**, 5, 409.
17. A. Corsini, D. Fowler, and M. Thompson, *Anal. Chim. Acta*, **1976**, 86, 237.
18. Y. Kushi and Q. Fernando, *J. Am. Chem. Soc.*, **1970**, 92, 91.
19. L. M. Leung, W. Y. Lo, S. K. So, K. M. Lee, and W. K. Choi, *J. Am. Chem. Soc.*, **2000**, 122, 5640.
20. I. Yamaguchi, T. Iijima, and T. Yamamoto, *J. Organometal. Chem.*, **2002**, 654, 229.
21. M. Brinkmann, G. Gadret, M. Muccini, C. Taliani, N. Masciocchi, and A. Sironi, *J. Am. Chem. Soc.*, **2000**, 122, 5147.
22. A. Yuchi, M. Shiro, H. Murakami, H. Wada, and G. Nakagawa, *Bull. Chem. Soc. Jpn.*, **1990**, 63, 677.
23. A. Yuchi, H. Murakami, M. Shiro, H. Wada, and G. Nakagawa, *Bull. Chem. Soc. Jpn.*, **1992**, 65, 3362.
24. A. Yuchi, H. Muranaka, S. Yamada, and M. Tanaka, *Bull. Chem. Soc. Jpn.*, **1980**, 53, 1560.