Low cost, high sensitivity detection of waterborne Al^{3+} cations and F^- anions via the fluorescence response of a morin derivative dye

Alhulw Alshammari[1,2]*, Zahrah Alqahtani[2], Faiz Bukhari Mohd Suah[3], Syaza Atikah Nizar[3], Alan Dunbar[4], Martin Grell[2]
[1]Physics department, College of Science, Jouf University, P.O. Box:2014, Sakaka, Saudi Arabia
[2]Department of Physics and Astronomy, University of Sheffield, Hicks Building, Hounsfield Rd, Sheffield S3 7RH, United Kingdom.
[3]School of Chemical Sciences, Universiti Sains Malaysia (USM), 11800, Minden, Pulau Pinang, Malaysia.
[4]Department of Chemical and Biological Engineering, The University of Sheffield, Mappin St, Sheffield S1 3JD, UK.

*ahalshammari@ju.edu.sa

Abstract :

Morin dye is known as a cheap and readily available selective 'off / on' fluorescent sensitiser when immobilised in a phase transfer membrane for the detection of Al^{3+} ions. Here, a morin derivative, NaMSA, which readily dissolves in water with good long-term stability is used in conjunction with a fibre optic transducer with lock-in detection to detect Al^{3+} in drinking water below the potability limit. The combination of a water soluble dye and the fibre optic transducer require neither membrane preparation nor a fluorescence spectrometer yet still display a high figure-of- merit. The known ability to recover morin-based Al^{3+} cation sensors selectively by exposure to fluoride (F^-) anions is further developed enabling a complementary sensing of either fluoride anions, or aluminium cations, using the same dye with a sub-micromolar limit-of-detection for both ions. The sensor performance parameters compare favourably to prior reports on both aqueous aluminium and fluoride ion sensing.

1. Instrument and materials

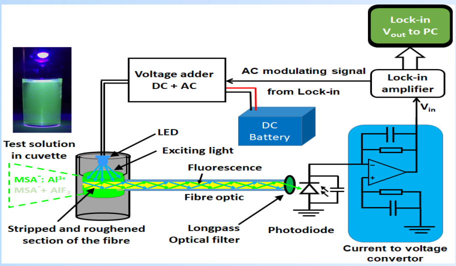

Fig. 1: *Schematic diagram of our fibre- optic lock-in fluorimeter*

Morin was purchased from Sigma Aldrich and chemically modified into the water- soluble sodium salt of morin sulfonic acid (NaMSA) by Faiz et al. [1]

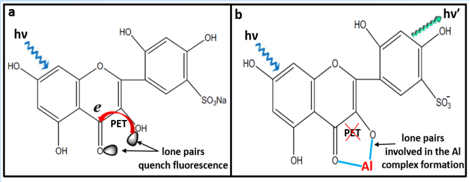

Fig.2: *a.) Chemical Structure of NaMSA when dissolved in water, this dissociates into MSA^- and Na^+. b.) Structure of $[MSA^-:Al^{3+}]$ complex that forms in aqueous solution when Al^{3+} is added to dissolved NaMSA.*

2. Result and discussion:

- Light intensity is transduced into a lock-In output voltage (**V_{out}**).

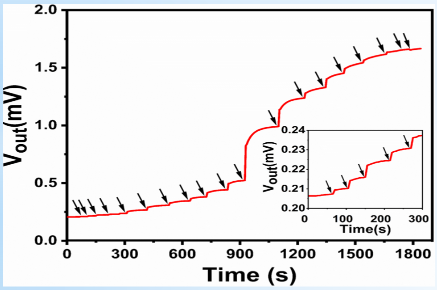

Fig. 3: *Example of a V_{out} vs time series for NaMSA solution under stepwise additions of Al^{3+} aliquots. Every arrow indicates a titration step, i.e. addition of an Al^{3+} aliquot. Inset: Magnification of the short time / low Al^{3+} concentration region.*

2.1 Sensor Calibration for 'off → on' Al^{3+} Sensors

The $V_{out}(t)$ data recorded during titrations shown in Fig. 3. were converted into $V_{out}(c)$ by relating the time to ion concentration, c. For further analysis of $V_{out}(c)$ which is proportional to I(c), where I(c) is the fluorescence intensity, we assume the fraction θ(c) of the dye complexed by the analyte at an analyte concentration c is given by a Langmuir-like relationship:

$$\theta(c) = \frac{kc}{(kc+1)} \qquad (1)$$

(c) is given by the relative fraction of complexed dye, θ(c):

$$V_{out}(c) = V_\infty \ \theta(c) = V_\infty \frac{kc}{kc+1} \qquad (2)$$

Wherein $V_\infty = V_{out}(c \rightarrow \infty)$. To determine k (stability constant), we therefore fitted the experimental $V_{out}(c)$ data to Eq.2 using the non-linear fit routine in Origin 2018 software as shown in Fig. 4.

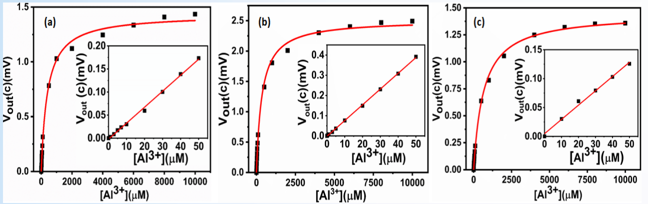

Fig. 4. *$V_{out}(c)$ as a measure of the fluorescence intensity of NaMSA in (DI-water/ HCl), pH = 5, shown against Al^{3+} concentration from 1 μM to 10 mM, the solid line is the fit to the data using Eq. 2 . The insets magnify the linear regime for $[Al^{3+}]$ up to 50 μM. a.) fresh 200 μM NaMSA solution and using the PMMA cuvette, b.) fresh 200 μM NaMSA solution and using the stainless steel cuvette, and c.) two months old NaMSA solution and using the PMMA cuvette.*

The resulting sensor parameters are evaluated and summarised in table 1.

Table 1.

	V_∞ [mV]	k_c [L/mol]	m [L/mol mV]	b [mV]	Δb [mV]	LoD [μM]
PMMA cuvette	1.43	2460	3460	-0.0021	0.0015	1.3
200 μM NaMSA	± 0.02	± 160	± 60			
Steel cuvette	2.51	2800	7790	-0.0018	0.0011	0.4
200 μM NaMSA	± 0.03	± 180	± 50			
PMMA cuvette	1.45± 0.02	1520	2470	0.0025	0.0032	3.84
old 200 μM NaMSA		± 80	± 100			

Table 1. *Parameters obtained from fitting the data in fig.4 to Eq. 2*

2.2 Sensor Calibration for 'on→ off' F^- Sensors

For the sensing of F^- with $[Al^{3+}:MSA^-]$ complex, the $V_{out}(c)$ is given by the fraction of remaining $[Al^{3+}:MSA^-]$ complex, 1 - θ(c):

$$V_{out}(c) = V_0\,[1 - \theta(c)] = \frac{V_0}{(kc+1)} \qquad (3)$$

Wherein $V_0 = V_{out}(c = 0)$. To determine k, we therefore fitted the experimental $V_{out}(c)$ data to Eq. 3. To evaluate the LoD for an 'on → off' dye we again consider only data at 'small' concentrations, c << 1/k, where Eq. 3 can be approximated by Eq. 4:

$$V_{out}(c) \approx V_0\,(1 - kc) \Rightarrow 1 - V_{out}(c)/V_0 \approx kc \text{ for } c \ll 1/k \qquad (4)$$

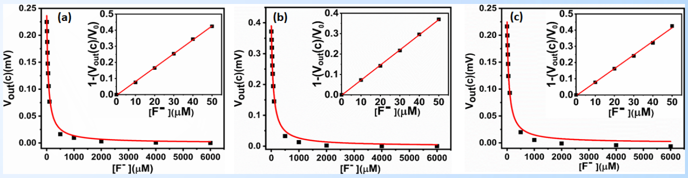

Fig. 5. *$V_{out}(c)$ as a measure of the fluorescence intensity of NaMSA dissolved in (DI water / HCl), pH = 5, and activated with 50 μM of Al^{3+}, shown against F^- concentration from 10 μM to 6 mM. The insets show the linear regime of $1-(V_{out}(c)/V_0)$ vs F^- for concentrations up to 50 μM. The three plots are a.) fresh 200 μM NaMSA solution as measured in the PMMA cuvette, b.) fresh 200 μM NaMSA solution as measured in the stainless steel cuvette, and c.) two months old NaMSA measured in a PMMA cuvette.*

The sensor parameters are evaluated and summarised in table 2.

Table 2.

	V_0[mV]	k_{dc} [L/mol]	m [L/mol]	b	Δb	LoD [μM]
PMMA cuvette	0.236	16400	8610	-0.0047	0.00322	1.1
200 μM NaMSA	±0.006	±1500	± 10			
Steel cuvette	0.390	13800	7410	-0.0023	0.00212	0.9
200 μM NaMSA	±0.010	±1290	± 70			
PMMA cuvette	0.225	14210	8400	-0.0084	0.006	2.1
aged 200 μM NaMSA	± 0.006	±1470	± 197			

Table 7.3. *Parameters such as the de-complexation constant K_{dc}, slope m, and LoD obtained from fitting data in fig. 5 (a to c) to Eq.4.*

2.3 Selectivity for Fluoride over Chloride

We have tested the selectivity of the $[MSA^-:Al^{3+}]$ complex as a sensitiser for fluoride by considering chloride as a potential interferant. In Fig. 5 we compare fluoride and chloride titrations under otherwise identical conditions.

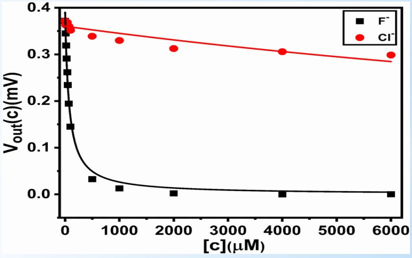

Fig. 6. *$V_{out}(c)$ as a measure of the fluorescence of 200 μM NaMSA solution in acidified water activated with 50 μM of Al^{3+} shown against F^- and Cl^- concentration.*

2.4 Comparison to Prior Fluorimetric Al^{3+} and F^- Sensors

Table 3.

No.	Analyte	k [L/mol]	LoD [M]	FoM	Medium	Ref.
1	Al^{3+}	$k_c = 5 \times 10^3$	1×10^{-6}	200	DMF / HEPES	[2]
2	Al^{3+}	$k_c = 3.68 \times 10^4$	1×10^{-6}	27	MeCN / Water	[3]
3	Al^{3+}	$k_c = 1.84 \times 10^4$	2.3×10^{-7}	236	Buffer solution	[4]
4	Al^{3+}	$k_c = 1 \times 10^5$	6×10^{-7}	17	DMSO / Water	[5]
5	Al^{3+}	$k_c = 9.87 \times 10^4$	3×10^{-8}	337	HEPES buffer	[6]
6	Al^{3+}	$k_c = 8.5 \times 10^5$	1.05×10^{-8}	112	DMSO / Water	[7]
7	Al^{3+}	$k_c = 5 \times 10^6$	1.35×10^{-9}	148	DI Water	[8]
8	Al^{3+}	$k_c = 2.8 \times 10^3$	4×10^{-7}	893	Acidified DI Water	This work
9	F^-	$k_c = 4.69 \times 10^4$	5.8×10^{-7}	37	MeCN	[9]
10	F^-	-------------	9×10^{-6}	------	DMSO	[10]
11	F^-	$k_c = 1 \times 10^4$	2.43×10^{-6}	41	$CHCl_3$	[11]
12	F^-	$k_{dc} = 1.38 \times 10^4$	9×10^{-7}	81	Acidified DI Water	This work

Table 3. *Performance parameters of different fluorimetric Al^{3+} and F^- sensors. Collated from the literature, and from tables 1 and 2 for values measured in this work. The abbreviations used for the different media refer to MeCN: Acetonitrile, DMSO: Dimethylsulfoxide, DMF: Dimethylformamide, and $CHCl_3$: Chloroform*

3. Conclusion

- We extend the use of morin or its derivatives as an Al^{3+} selective 'off → on' fluorescent sensitiser when immobilised in a phase transfer membrane to a morin derivative, NaMSA, dissolved in water, avoiding the need for membrane preparation.
- A fibre optic transducer to demonstrate Al^{3+} detection in drinking water well below the potability limit was developed.
- Further, by exposure to fluoride (F^-) anions the Al^{3+} cation sensors can be recovered. Here, we also utilise the selective recovery of the dissolved NaMSA- Al^{3+} complex by exposure to F^- to develop a fully 'complementary' sensor for either aluminium cations, or fluoride anions, with LoDs below the potability limit for both of these important water pollutants. Dissolved NaMSA works as an 'off →on' sensor for Al^{3+} cations. We propose that other ion selective dyes with known recovery agents could be used in a similar manner to produce a wide range of low cost complementary ion sensors.
- The lock-in fibre optic transducer concept developed in this work is recommended as an alternative to conventional spectrofluorimeters, which can demonstrate a higher figure- of- merit at lower footprint.

Acknowledgements: Alhulw Alshammari thanks jouf University, Saudi Arabia, for funding this work

References:

[1] F. B. M. Suah and M. Ahmad, "Preparation and characterization of polymer inclusion membrane based optode for determination of Al3+ ion," *Anal. Chim. Acta*, vol. 951, pp. 133-139, Jan. 2017. [2] K. B. Kim, D. M. You, J. H. Jeon, Y. H. Yeon, J. H. Kim, and C. Kim, "A fluorescent and colorimetric chemosensor for selective detection of aluminum in aqueous solution," *Tetrahedron Lett.*, vol. 55, no. 7, pp. 1347-1352, 2014.
[3] V. P. Singh, K. Tiwari, M. Mishra, N. Srivastava, and S. Saha, "5-[{(2-Hydroxynaphthalen-1-yl)methylene}amino]pyrimidine-2,4(1H,3H)-dione as Al3+ selective colorimetric and fluorescent chemosensor," *Sensors Actuators, B Chem.*, vol. 182, pp. 546-554, 2013.
[4] B. In, G. W. Hwang, and K. H. Lee, "Highly sensitive and selective detection of Al(III) ions in aqueous buffered solution with fluorescent peptide-based sensor," *Bioorganic Med. Chem. Lett.*, vol. 26, no. 18, pp. 4477-4482, 2016.
[5] Z. Kejík *et al.*, "Aluminium(III) sensing by pyridoxal hydrazone utilising the chelation enhanced fluorescence effect," *J. Lumin.*, vol. 180, pp. 269-277, 2016.
[6] J. Y. Xie, C. Y. Li, Y. F. Li, Y. J. Fu, S. X. Nie, and H. Y. Tan, "A near-infrared chemosensor for determination of trivalent aluminum ions in living cells and tissues," *Dye. Pigment.*, vol. 136, pp. 817-824, 2017.
[7] D. Sarkar, P. Ghosh, S. Gharami, T. Kumar, and N. Murmu, "A novel coumarin based molecular switch for the sequential detection of Al3+ and F−: Application in lung cancer live cell imaging and construction of logic gate," *Sensors Actuators B. Chem.*, vol. 242, pp. 338-346, 2017.
[8] R. Dwivedi *et al.*, "Intracellular application and logic gate behavior of a 'turn off-on-off' type probe for selective detection of Al3+ and F− ions in pure aqueous medium," *Sensors Actuators, B Chem.*, vol. 258, pp. 881-894, 2018.
[9] B. Bhattacharyya, A. Kundu, N. Guchhait, and K. Dhara, "Anthraimidazoledione Based Reversible and Reusable Selective Chemosensors for Fluoride Ion: Naked-Eye, Colorimetric and Fluorescence 'ON-OFF,'" *J. Fluoresc.*, vol. 27, no. 3, pp. 1041-1049, 2017.
[10] J. Y. Xie *et al.*, "A novel colorimetric and fluorescent probe for detecting fluoride anions: From water and toothpaste samples," *Dye. Pigment.*, vol. 55, no. 7, pp. 4477-4482, 2016.
[11] D. Thongkum and T. Tuntulani, "Fluoride-induced intermolecular excimer formation of bispyrenyl thioureas linked by polyethylene glycol chains," *Tetrahedron*, vol. 67, no. 42, pp. 8102-8109, 2011.
[12] G. Sposito, *The Enviromental chemistry of aluminum.* CRC Press, 1995.