RSC Advances

RSC Advances

ARTICLE TYPE

Selective sensing of Al³⁺ by naphthyridine coupled rhodamine chemosensors

Kumaresh Ghosh[*], Anupam Majumdar and Tanmay Sarkar

Napthyridine-based rhodamine chemosensors **1** and **2** have been designed and synthesized. Both the chemosensors selectively recognize Al³⁺ ion over a series of other cations in CH_3CN-H_2O (4:1, v/v, 10 μM tris HCl buffer, pH = 7.0) by exhibiting change in color (colorless to pink) and emission at 588 nm in turn on mode. Complexation is reversible and the ensembles of **1**.Al³⁺ and **2**.Al³⁺ selectively sense F⁻ ion by discharging pink color of the solutions and bring reverse change in both absorption and emission spectra.

Introduction

Aluminium ion is the third abundant metal ion found in nature and exists in its ionic form Al³⁺ ion.[1] It is extensively used in modern life, such as food packaging, cookware, drinking water supplies, antiperspirants, deodorants, antacids and manufacturing of cars and computers. Aluminium ion enters into human body through food and water.[2] Average daily intake of Al³⁺ ions for human body is about 3-10 mg/day.[3] Excess amount of Al³⁺ is neurotoxic to humans and can cause a wide range of diseases, such as, Alzheimer's disease, Parkinson's disease, osteoporosis etc.[4] In addition, the incremental increase of Al³⁺ in environment is detrimental to growing plants. Due to poor coordinating ability of Al³⁺ ion, its detection by highly selective and sensitive chemosensors is of great interest for human health and environment.

In continuation of our work on sensing of cations[5] of biological and environmental importance, we report in this full account, two receptor modules **1**[6] and **2** which are naphthyridine based. Both the receptors **1** and **2** show high selectivity towards Al³⁺ ion in CH_3CN-H_2O (4:1, v/v, 10μM tris HCl buffer, pH = 7.0) by exhibiting color and emission changes.

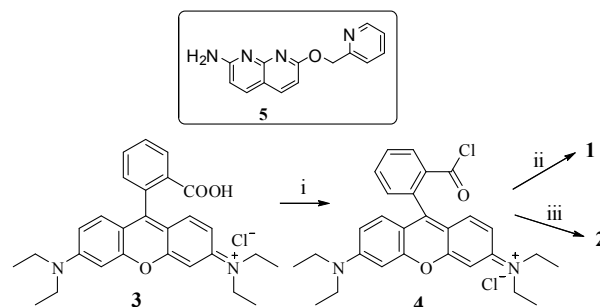Rhodamine B and its derivatives (RhB) show good photo stability, high extinction coefficient (>75000 cm¹ M⁻¹), and high fluorescence quantum yield.[7] The performance of this moiety in sensing metal ion is linked with the switching of the spirocyclic form (which is colorless and non fluorescent) to the opened ring amide form which is pink in color and strongly fluorescent. Metal ion recognition using rhodamine labeled chemosensors is recently

thoroughly reviewed.[8] A less number of rhodamine labeled chemosensors which show color change and selective "turn-on" emission to Al³⁺ ions is reported in the literature.[9] In the design 1,8-naphthyridine has been exploited because of its intriguing structure and bonding properties. It is a well established motif and thus applied in coordination chemistry[10], pharmaceutical[11] and molecular recognition fields.[12]
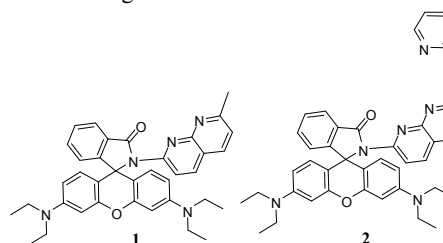
Results and discussion

The chemosensors **1** and **2** were accomplished according to the Scheme 1. During the course of our study on **1** in cation recognition, Kong *et al*., recently reported the synthesis of **1** and its anion sensing behavior.[6] However, in our method, initially

Department of Chemistry, University of Kalyani, Kalyani-741235, India. Email: ghosh_k2003@yahoo.co.in, Fax: +913325828282; Tel: +913325828750.

Scheme 1. (i) $POCl_3$, $ClCH_2CH_2Cl$, reflux, 2h; (ii) 2-Amino-7-methyl-1,8-naphthyridine, Et_3N, dry CH_2Cl_2, 10h; (iii) **5**, Et_3N, dry CH_2Cl_2, 12h.

rhodamine **3** was converted to the acid chloride **4** which was reacted with 2-amino-7-methyl-1,8-naphthyridine[13] in the presence of Et_3N in dry CH_2Cl_2 to afford the desired compound **1** in appreciable yield. Following the same strategy, compound **2** was prepared by coupling the acid chloride **4** with the compound **5** in dry CH_2Cl_2. The intermediate compound **5**[14] was obtained according to our reported procedure. All the compounds were fully characterized by ^1H, ^{13}C, FTIR, and mass analyses.

The metal ion sensing properties of **1** and **2** towards the metal ions such as Al^{3+}, Cr^{3+}, Fe^{3+}, Hg^{2+}, Co^{2+}, Pb^{2+}, Cu^{2+}, Ni^{2+}, Mg^{2+}, Zn^{2+}, Cd^{2+} and Ag^+ were evaluated in $CH_3CN/$ H_2O (CH_3CN: H_2O = 4: 1, v/v,10 μM tris HCl buffer, pH = 7.0). Without metal ions, both the chemosensors **1** and **2** were almost non fluorescent. However, on excitation either at 480 nm (Fig. S1 and Fig. S2, ESI) or at 510 nm, both **1** and **2** showed emission at 588 nm with significant intensity upon interaction with Al^{3+} ions (Fig. 1). Other cations in the study brought insignificant change in emission at this wavelength for sensors **1** and **2** (Fig. S1 and Fig. S2, ESI). Upon interaction with Al^{3+}, the colourless solutions of **1** and **2** turned into pink color. In reality, addition of small amount of Al^{3+} to the solution of **2** caused greater change in emission than the case with **1**. This indicated the better sensitivity of **2** than **1** in Al^{3+} detection.
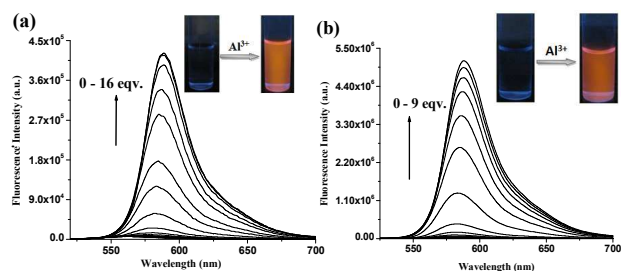

Fig. 1 Fluorescence titration spectra of (a) **1** (c = 3 x 10^{-5} M) and (b) **2** (c = 3 x 10^{-5} M) in CH_3CN/water (4/1, v/v; 10 μM tris HCl, pH = 7.0) upon addition of $Al_2(SO_4)_3$.18H_2O (c = 1.2 x 10^{-3} M). Insets represent color changes of the receptor solutions under illumination of UV light.

Figure 2 shows the change in fluorescence ratios $[(I-I_0)/I_0]$ of **1** and **2** at 588 nm in the presence of 16 equiv. and 9 equiv. amounts of different metal ions, respectively.
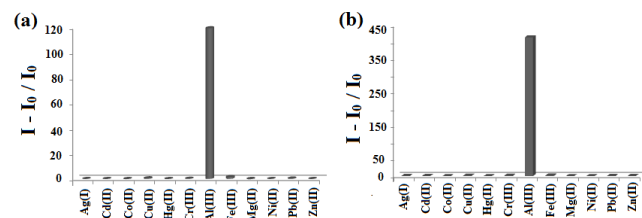

Fig. 2 Fluorescence ratios $[(I-I_0)/I_0]$ at 588 nm of (a) **1** (c = 1.5 x 10^{-5} M) and (b) **2** (c = 1.5 x 10^{-5} M) in CH_3CN/water (4/1, v/v; 10 μM tris HCl buffer, pH 7.0) upon addition of 16 equiv. and 9 equiv. amounts of metal ions respectively.

UV-vis titration of **1** (c = 3 x 10^{-5} M) in CH_3CN/H_2O (4/1, v/v; 10 μM tris HCl buffer; pH= 7.0) with Al^{3+} resulted in sharp ratiometric change in absorbance. The absorption at 274 nm and 322 nm gradually decreased along with appearance of new peak at 559 nm (Fig. 3a). Other metal ions taken in the study did not produce such change in absorbance (Fig. S3, ESI). A similar type of spectral behaviour was observed in case of **2** (Fig. 3b). Like the case of **1**, other metal ions did not bring much change in absorbance of **2** (Fig. S4, ESI).

Indeed, appearance of the peak at 559 nm in UV-vis and 588 nm in emission is due to opening of spirolactam rings in **1** and **2** to form metal chelated equilibrium structures **1A** and **2A** (Fig. 4). The amide carbonyl stretching appeared at 1705 cm^{-1} in **1** was observed at 1658 cm^{-1} upon complexation of Al^{3+}. Similarly, the carbonyl stretching appeared at 1696 cm^{-1} in **2** moved to 1648 cm^{-1} upon complexation. This significant reduction in carbonyl stretching substantiated the lactam ring opening in the interaction process. Thus, napthyridine and lactam anion in **1** participate in chelation of Al^{3+} ion. In **2**, contribution of the extra pyridine ring
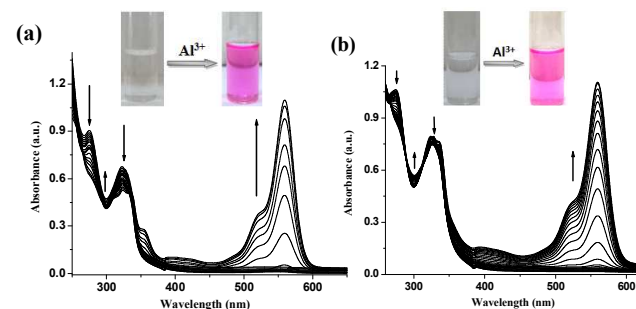

Fig. 3 (a) UV-vis titration spectra of **1** (c = 3 x 10^{-5} M) in CH_3CN/H_2O (4/1, v/v; 10 μM tris HCl buffer; pH 7.0) upon addition of $Al_2(SO_4)_3$.18H_2O (c = 1.2 x 10^{-3} M). Inset: Color change upon addition of Al^{3+} ions (c = 1.2 x 10^{-3} M) and (b) UV-vis titration spectra of **2** (c = 3 x 10^{-5} M) in CH_3CN/H_2O (4/1, v/v; 10 μM tris HCl buffer; pH 7.0) upon addition of $Al_2(SO_4)_3$.18H_2O (c = 1.2 x 10^{-3} M). Inset: Color change upon addition of Al^{3+} ions (c = 1.2 x 10^{-3} M).

attached to naphthyridine is noteworthy for its strong complexation and greater sensitivity towards Al^{3+} ion. DFT[15] optimized geometry in Fig. 5 clearly depicts the participation of naphthyridine, pyridine and the lactam moieties in complexation of Al^{3+} ion.
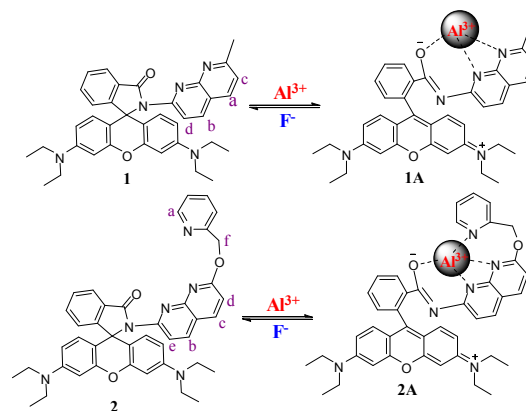

Fig. 4 Suggested metal chelated structures.

Further to substantiate the binding, ^1H NMR spectra of both **1** and **2** in the absence and presence of Al^{3+} ion were recorded. As can

be seen from Fig. 6, the naphthyridine ring protons in both cases exhibited downfield chemical shift on complexation of Al^{3+} ion. The signal for the $-CH_2-$ group, adjacent to pyridine ring, also moved downfield and thus supported the additional involvement of the pyridine ring in complexation. The change in chemical shift values has been shown in the caption of Fig. 6.
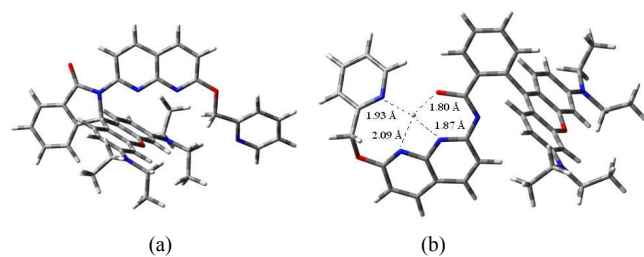

Fig. 5 DFT optimized geometries (using b3lyp functional and 6-31G basis set) of (a) **2** and (b) its complex with Al^{3+}.

In the interactions, the stoichiometries[16] of **1** and **2** were evaluated to be 1:1 (Fig. S5, ESI) and the binding constant[17] values were determined to be $(5.39 \pm 0.01) \times 10^3$ M^{-1} and $(6.5 \pm 0.009) \times 10^3$ M^{-1} for **1** and **2**, respectively (Fig. S6, ESI). Due to poor change in emission titration, we were unable to determine
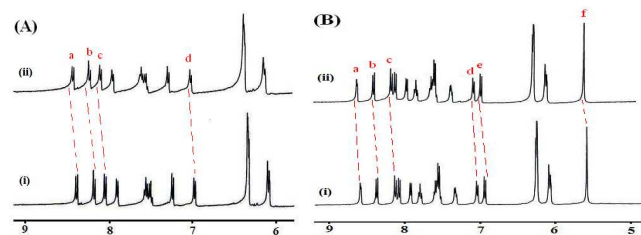

Fig. 6 (A) ^1H NMR (d_6–DMSO, 400 MHz) of (i) **1** ($c = 8.6 \times 10^{-3}$ M), (ii) **1** with 1 equiv. amount of $Al_2(SO_4)_3.18H_2O$ ($\Delta\delta$ in ppm: $H_a = 0.30$, $H_b = 0.26$, $H_c = 0.02$, $H_d = 0.05$) and (B) ^1H NMR (d_6–DMSO, 400 MHz) of (i) **2** ($c = 8.9 \times 10^{-3}$ M), (ii) **2** with 1 equiv. amount of $Al_2(SO_4)_3.18H_2O$ ($\Delta\delta$ in ppm: $H_a = 0.05$, $H_b = 0.05$, $H_c = 0.06$, $H_d = 0.10$, $H_e = 0.05$, $H_f = 0.06$) [for identification of protons see the labeled structures in Fig. 4].

the binding constant values for other metal ions. However, the binding constant values for Al^{3+} ion indicate that the contribution of pyridine in **2** to the stability of the metal complex is not significantly high. But in practice, the sensitivity level of **2** is greater than **1**. Analysis of the fluorescence titration data gave the detection limits[18] 2.94×10^{-5} M and 1.38×10^{-5} M for **1** and **2**, respectively (Fig. S7, ESI).

To understand the selectivity in the sensing process, the change in emission of **1** was observed in the presence and absence of other metal ions. No metal ion considered in the study interfered in the binding of Al^{3+} (Fig. 7a). Similar results were observed for **2** (Fig. 7b). It is important to be mentioned that the chemosensors **1** and **2** gave the same results with $AlCl_3$ and K_2SO_4. $Al_2(SO_4)_3$. $24H_2O$ under similar conditions (Fig S8, ESI) and thereby ruled out the possibility of any role of anionic part of the aluminium salts in the sensing process.

Further to check the reversibility in complexation, halide added experiment was performed. Addition of F^- to the ensembles of **1** and **2** with Al^{3+} brought about the reverse change in the absorption as well as in emission spectra (Fig. 8). In contrast,
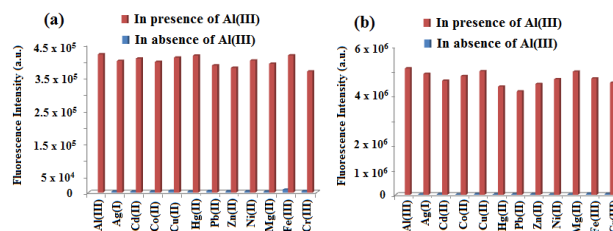

Fig. 7 Fluorescence responses of (a) **1** ($c = 3 \times 10^{-5}$ M) and (b) **2** ($c = 3 \times 10^{-5}$ M) towards Al^{3+} ($c = 1.2 \times 10^{-3}$ M) over the selected metal ions ($c = 1.2 \times 10^{-3}$ M).

other halides taken in the study were unable to decomplex Al^{3+} ions from the complexes **1A** and **2A**. Stronger affinity of F^- towards Al^{3+} ions caused complete decomplexation and retrieved the spiro lactam rings of **1** and **2** for which the pink color of the ensembles was completely discharged (Fig. 9). Thus the ensembles are useful in the selective recognition of F^- over the other halides. Fluoride recognition is an important topic in supramolecular chemistry research for its biological significance.[19]
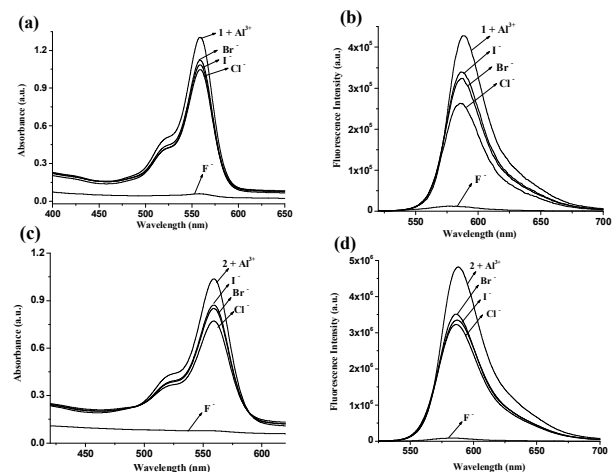
Fig. 8 Changes in (a) absorbance and (b) emission of **1**-Al^{3+} complex in CH_3CN/H_2O (4/1, v/v; 10 μM tris HCl buffer; pH 7.0) upon addition of different halides ($c = 3 \times 10^{-3}$ M); Changes in (c) absorbance and (b) emission of **2**-Al^{3+} complex in CH_3CN/H_2O (4/1, v/v; 10 μM tris HCl buffer; pH 7.0) upon addition of different halides ($c = 3 \times 10^{-3}$ M).
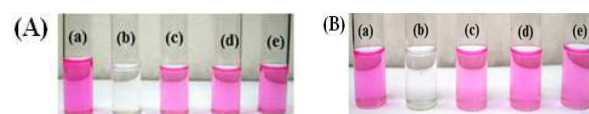
Fig. 9 (A) Color changes of ensemble **1**.Al^{3+} in CH_3CN/H_2O (4/1, v/v; 10 μM tris HCl buffer; pH 7.0), after addition of 250 μl ($c = 3 \times 10^{-3}$ M) of each halide solution: (a) **1**.Al^{3+} ensemble, (b) **1**.Al^{3+} + F^-, (c) **1**.Al^{3+} + Cl^-, (d) **1**.Al^{3+} + Br^- and (e) **1**.Al^{3+} + I^-, (B) Color change of ensemble **2**.Al^{3+} in CH_3CN/H_2O (4/1, v/v; 10 μM tris HCl buffer; pH 7.0), after addition of

200 μl (c = 3x10^{-3} M) of each halide solution: (a) **2**.Al^{3+} ensemble, (b) **2**.Al^{3+} + F$^-$, (c) **2**.Al^{3+} + Cl$^-$, (d) **2**.Al^{3+} + Br$^-$ and (e) **2**.Al^{3+} + I$^-$.

Conclusion

In conclusion, naphthyridine-based rhodamine sensors **1** and **2** selectively and effectively recognize Al^{3+} ion over a series of other cations in aqueous CH$_3$CN at pH 7.0 by exhibiting sharp change in color and emission in turn on mode. The ensembles of the sensors **1** and **2** with Al^{3+} further recognize F$^-$ ions selectively through a change in color (pink to colorless) as well as emission in turn off fashion. The chemosensors in this account are the new addendum to the existing few reports on aluminium sensor in the literature.[9]

Experimental

Synthesis
Compound 1:
To a stirred solution of rhodamine B (0.15 g, 0.313 mmol) in 1,2-dichloroethane (10 mL) phosphorus oxychloride (300 μL) was added dropwise at room temperature. The resulting solution was refluxed for 2h. The reaction mixture was cooled to room temperature and excess solvent was evaporated off in vacuo to give rhodamine B acid chloride **4**, which was impure and used in the next step directly. The crude acid chloride **4** was dissolved in dry CH$_2$Cl$_2$ (10 mL) and was added dropwise over 10 mins to the solution of 2-amino-7-methyl-1,8-napthyridine (0.06 g, 0.408 mmol) in CH$_2$Cl$_2$ (10 mL) containing Et$_3$N (100 μL). The reaction mixture was stirred at room temperature for 10 h. After completion of reaction, solvent was removed under reduced pressure. Water was added to the residue and product was extracted with chloroform (20 mL x 3), dried over anhydrous Na$_2$SO$_4$. Evaporation of the solvent gave the crude product which was purified by silica gel column chromatography using petroleum ether : ethyl acetate (7:3, v/v) as eluent to give pure compound **1** (0.06 g, 32%), mp 192^{0}C, ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.15 (d, 1H, J = 8 Hz), 8.03 (d, 1H, J = 8 Hz), 7.90 (d, 1H, J = 8 Hz), 7.81 (d, 1H, J = 8 Hz), 7.51 – 7.46 (m, 2H), 7.12 (d, 2H, J = 8 Hz), 6.60 (d, 2H, J = 8 Hz), 6.45 (d, 2H, J = 2.4 Hz), 6.16 (dd, 2H, J_1 = 8 Hz, J_2 = 2.4 Hz), 3.30 - 3.25 (m, 8H), 2.66 (s, 3H), 1.11 (t, 12H, J = 8 Hz); ^{13}C NMR (100 MHz, CDCl$_3$): δ 169.0, 162.3, 154.4, 154.3,153.0, 152.7, 148.4, 137.3, 136.1, 133.9, 129.1, 128.1, 127.8, 124.1, 123.5, 121.5, 118.3, 116.3, 107.8, 107.5, 97.9, 66.7, 44.2, 29.7, 12.6; FT-IR: ν cm^{-1} (KBr): 2767, 2918, 1705, 1614, 1513, 1503; HRMS (ESI): calcd. C$_{37}$H$_{39}$N$_5$O$_2$ [M + 2H]$^{2+}$ 292.6552, found 292.6727; calcd. [M + H]$^+$ 584.3026, found 584.3334.

Compound 2:
The crude acid chloride **4** was dissolved in dry CH$_2$Cl$_2$ (10 mL) and was added dropwise over 10 mins to the amine **5**^{14a} (0.10 g, 0.396 mmol) taken in CH$_2$Cl$_2$ (10 mL) containing Et$_3$N (200 μL) and the reaction mixture was stirred for 12 h. After completion of reaction, solvent was removed under reduced pressure and the residue left was dissolved in water, extracted with CHCl$_3$ and dried over anhydrous Na$_2$SO$_4$. The crude mass was purified by silica gel column chromatography using petroleum ether : ethyl acetate (3:2, v/v) as eluent to yield the yellowish powdery compound **2** (0.08 g, 40%), mp 248^{0}C, ^{1}H NMR (400 MHz,

CDCl$_3$): δ 8.70 (d, 1H, J = 4 Hz), 8.37 (d, 1H, J = 8 Hz), 8.06 (d, 1H, J = 8 Hz), 7.85 (d, 1H, J = 8 Hz), 7.78 (d, 1H, J = 8 Hz), 7.75 (d, 1H, J = 8 Hz), 7.70 (d, 1H, J = 8 Hz), 7.54 (t, 2H, J = 8 Hz), 7.26 (d, 1H, J = 8 Hz), 7.20 (d, 1H, J = 8 Hz), 6.84 (d, 1H, J = 8 Hz), 6.50 (d, 2H, J = 8 Hz), 6.44 (d, 2H, J = 2.4 Hz), 6.14 (dd, 2H, J_1 = 8 Hz, J_2 = 4 Hz), 5.78 (s, 2H), 3.32 – 3.20 (m, 8H), 1.10 (t, 12H, J = 7.2 Hz); ^{13}C NMR (100 MHz, CDCl$_3$): δ 168.6, 163.6, 157.4, 154.1, 153.9, 153.4, 152.0, 149.3, 148.4, 138.3, 137.0, 136.6, 133.8, 130.0, 128.1, 127.8, 124.6, 123.2, 123.1, 122.5, 116.6, 113.6, 111.9, 108.4, 106.7, 97.9, 68.2, 66.9, 44.2, 12.6; FT-IR: ν cm^{-1} (KBr): 2966, 2727, 1696, 1603, 1514, 1495; HRMS (ESI): calcd. C$_{42}$H$_{42}$N$_6$O$_3$ [M + 2H]$^{2+}$ 339.1659, found 339.1875; calcd. [M + H]$^+$ 677.3240, found 677.3627.

References

1. (a) J. Barceló and C. Poschenrieder, *Environ. Exp. Bot.*, 2002, **48**, 75; (b) G. H. Robinson, *Chem. Eng. News*, 2003, **81**, 54; (c) The special issue on Aluminium: Lithosphere to Biosphere (and Back)", *J. Inorg. Biochem.*, 2005, **99**, 1747.

2. (a) D. R. Burwen, S. M. Olsen, L. A. Bland, M. J. Arduino, M. H. Reid and W. R. Jarvis, *Kidney Int.*, 1995, **48**, 469; (b) G. Berthon, *Coord. Chem. Rev.*, 2002, **228**, 319; (c) M. I. Yousef, A. M. A. EI-Morsy and M. S. Hassan, *Toxicology*, 2005, **215**, 97; (d) H. Bielarczyk, A. Jankowska, B. Madziar, A. Matecki, A. Michno and A. Szutowicz, *Neurochem. Int.*, 2003, **42**, 323.

3. (a) B. Valeur and I. Leray, *Coord. Chem. Rev.*, 2000, **205**, 3; (b) M. A. M. Rogers and D. G. Simon, *Age Ageing.*, 1999, **28**, 205; (c) Z. Krejpcio, R. W. Pol and J. Wojciak, *Environ. Stud.*, 2002, **11**, 251.

4. (a) D. P. Perl, D. C. Gajdusek, R. M. Garruto, R. T. Yanagihara and C. J. Gibbs, *Science.*, 1982, **217**, 1053; (b) D. P. Perl and A. R. Brody, *Science*, 1980, **208**, 297; (c) E. Altschuler, *Med. Hypotheses.*, 1999, **53**, 22.

5. (a) K. Ghosh and T. Sen, *Beilstein J. Org. Chem.*, 2010, **6**, No. 44; (b) K. Ghosh and T. Sarkar, *Supramol. Chem.*, 2011, **23**, 435; (c) K. Ghosh, T. Sarkar and A. Samadder, *Org. Biomol. Chem.*, 2012, **10**, 3236; (c) K. Ghosh, T. Sarkar, A. Samadder and A. R. Khuda-Bukhsh. *New. J. Chem.*, 2012, **36**, 2121; (d) K. Ghosh, T. Sarkar and A. Majumdar, *Asian J. Org. Chem.*, 2013, **2**, 157; (e) K. Ghosh, T. Sarkar and A. Majumdar, *Anal. Methods*, **DOI:** 10.1039/C4AY00217B; (f) K. Ghosh, T. Sarkar and A. Majumdar, *Tetrahedron Lett.*, 2013, **54**, 6464.

6. K. Jichuan, H. Cheng, Z. Xiaolin, M. Qingtao and D. Chunying, *Dyes and Pigments*, 2014, **101**, 254.

7. R. P. Haugland, R. *The Handbook: A Guide to Fuorescent Probes and Labeling Technologies*, the Tenth Edition, Molecular Probes; Invitrogen Corp., Karlsbad, CA, 2005.

8. X. Chen, T. Pradhan, F. Wang, J. S. Kim and J. Yoon, *Chem Rev.*, 2012, **112**, 1910.

9. (a) S. B. Maity and P. K. Bharadwaj, *Inorg. Chem.*, 2013, **52**, 1161; (b) C. R. Lohani, J. M. Kim, S. Y. Chung, J. Yoon and K. H. Lee, *Analyst*, 2010, **135**, 2079; (c) Z. Li, Q. Hu, C. Li, J. Dou, J. Cao, W. Chen and Q. Zhu, *Tetrahedron Lett.*, 2014, **55**, 1258; (d) X. Fang, S. Zhang, G. Zhao, W. Zhang, J. Xu, A. Ren, C. Wu and W. Yang, *Dyes and Pigments*, 2014, **101**, 58; (e) Y. Mi, Z. Cao, Y. Chen, S. Long, Q. Xie, D. Liang, W. Zhu and J. Xiang, *Sensors and Actuators B*, 2014,

192, 164; (f) F. Yan, M. Wang, D. Cao, N. Yang, Y. Fu, L. Chen and L. Chen, *Dyes and Pigments*, 2013, **98**, 42.

10. (a) M.-M. Yu, Z, -X. Li, L. –H. Wei, D. –H. Wei and M. –S. Tang, *Org. Lett.,* 2008, **10**, 5115 and references cited therein; (b) G. Pace, A. Petitjean, M. –N. Lalloz-Vogel, J. Harrowfield, J.-M. Lehn and P. Samori, *J. Org. Chem.,* 2008, **73**, 2481; (c) B. –S. Liao, Y. –H. Liu, S. –M. Peng, K. Rajender Reddy, S. –H. Liu, P. –T. Chao and S. –T. Liu, *Dalton Trans*, 2014, **43**, 3557; (d) Y. G. Shi, Y. L. Duan, J. H. Chen, X. H. Wu, Y. Zhou and J. F. Zhang, *Bull. Korean Chem. Soc.,* 2013, **34**, 63; (e) A. Sinha, S. M. Wahidur Rahaman, M. Sarkar, B. Saha, P. Daw and J. K. Bera, *Inorg. Chem.,* 2009, **48**, 11114.

11. P. C. Appelbaum and P. A. Hunter, *International J. Antimicrobial Agents*, 2000, **16**, 5.

12. (a) K. Tanaka, M. Murakami, J. –H. Jeon, Y. Chujo, *Org. Biomol. Chem.,* 2012, **10**, 90; (b) M. Mazik, *RSC Adv.,* 2012, **2**, 2630.

13. (a) R. Ludwig, *Angew. Chem.,* 2001, **113**, 1856; (b) K. Ghosh and T. Sarkar, *J Incl. Phenom. Macrocycl. Chem.,* 2011, **71**, 243.

14. (a) K. Ghosh, T. Sen and R. Frohlich, *J Incl Phenom Macrocycl Chem.*, 2010, **68**, 193; (b) K. Ghosh, T. Sen and R. Frohlich, *Tetrahedron Lett.,* 2007, **48**, 2935.

15. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr. T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian 09 (Revision A.02), Gaussian, Inc., Wallingford CT, 2004.

16. P. Job, *Ann. Chim.*, 1928, **9**, 113.

17. B. Valeur, J. Pouget, J. Bourson, M. Kaschke and N. P. Eensting, *J. Phys.Chem.*, 1992, **96**, 6545.

18. A. Caballero, R. Martinez, V. Lloveras, I. Ratera, J. Vidal-Gancedo, K. Wurst, A. Tarraga, P. Molina and J. Vaciana, *J. Am. Chem. Soc.*, 2005, **127**, 15666.

19. R. Martinez-Manez and F. Sancenon, *Chem. Rev.*, 2003, **103**, 4419.