

A Self-Organized Ensemble of Fluorescent 3-Hydroxyflavone-Al (III) Complex as Sensor for Fluoride and Acetate Ions

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Abstract Aluminum chloride addition results in a self-organized TURN-ON fluorescence of 3-hydroxyflavone (3HF) by a complexation reaction in MeOH and subsequent ligand exchange reaction with fluoride or acetate ions causes a fluorescence TURN-OFF of this complex, delivering a quantitative estimation route for fluoride and acetate ions. The ternary complex of 3HF with Al (III), a hard acid provides for a sensitive signalling system for fluoride ion, a hard base in the concentration range from 6 μM to 50 mM by a concerted co-ordination of fluoride ion involving an intermediate mechanistic pathway, while the complex is sensitive to acetate addition between 0–68 μM . The ligand exchange reaction of Al (3HF)₂ complex by fluoride or acetate ion, without interference from other common anions, has been investigated by UV-visible and fluorescence spectroscopies. The structure of the in-situ intermediate isolated at higher Al (3HF)₂ complex and acetate concentrations was inferred from the FT-IR spectrum and ESI-MS of the sample.

Keywords 3-hydroxyflavone · AlCl₃ · Complexation · Ligand exchange · Fluoride · Acetate

Introduction

The design and development of sensors for important species, ions in environmental [1] and biological processes [2] is important [3] due to its vital health implications [4] and

hence is a frontier area of research in the field of supramolecular host-guest complexation chemistry. Currently available methods for anion detection include electrochemical (ion selective electrodes) [5, 6], chromatography [7] and chromogenic sensing systems [8, 9] involving spectrophotometry [10, 11]. Chromogenic sensors for anions consist of two parts: anion receptors and chromophores [12]. The different types of chromogenic anion sensors are classified based on their non-covalent interactions as, electrostatic [13], NH-based hydrogen bonding [14–16], Lewis acid [3, 4, 17, 18] and combinations of these interactions working together [1]. Of these wide array of available synthetic fluorescent sensors [1, 19, 20], few systems are capable of ion pair binding [21, 22]. While the organometallic metalacrown complex [23] acts as receptor for lithium fluoride, cryptands [24] have been used as ditopic fluorescent sensors for potassium fluoride. In contrast the self-organised systems directed by the displacement assay approach [25], provide for a simple analytical detection. The latest work here, involves the detection of anions [26] and metal ions [27] with the design of alizarin-phenylboronic acid ensembles.

An alternative approach designed by us, is a self-organized, one-pot, in-situ complexation reaction of AlCl₃ with 3-hydroxyflavone (3HF) in MeOH that provides for a fluoride and acetate ion sensor through a ligand exchange reaction. 3HF, a flavonoid compound plays an important role as an antioxidant and metal ion chelator [28]. The chelating pattern and power of the 3-hydroxy-4-keto functional group in 3HF has been well studied and characterized with Al(III), Fe(III), Pb(II) and Zn(II) [29–32] involving high stability constants, resulting in stable in-situ metal complexes. Consequently, 3HF has been used as a biological and pharmaceutical agent [33] by its ability to act as free radical acceptor and regulate the bioavailability and toxicity of a

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variety of metals. Our novelty lies in the extension of this cation binding ability of flavonoids resulting in complexes to sense fluoride and acetate ions in MeOH medium, as no report on the use of this in-situ, 3HF-aluminum complex for anion sensing, has appeared so far. This communication deals with the absorption and fluorescence TURN-OFF of the 3HF-aluminum complex by fluoride and acetate ions in MeOH. The concept and data presented provide an insight for the design of novel self-organized, one-pot molecular sensors and brings to light a new field of fluoride and acetate sensors that are still unexplored.

3HF molecule forms an Al (3HF)₂ complex in pure methanol as confirmed by spectrophotometric and quantum semi-empirical AM1 methods [29]. Conceivably, this Lewis acid-base complexation reaction triggered a fluorescence TURN-ON of 3HF. The high affinity of hard Lewis acid, Al(III) to hard Lewis base, fluoride [34–36] (or acetate ion) and the fluorescence characteristics of Al (3HF)₂ complex have been successfully utilized for fluoride and acetate detection by a fluorescence TURN-OFF ligand exchange reaction.

Experimental

Materials

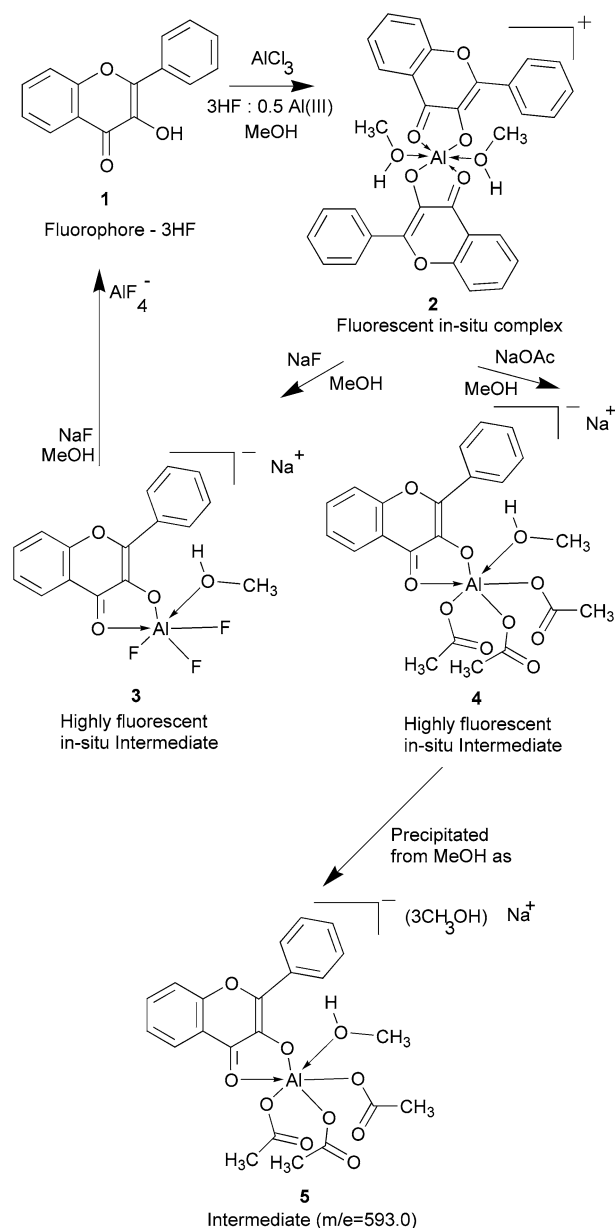
All chemicals were purchased from Sigma. 3HF was recrystallized three times from MeOH. AlCl₃, NaF, NaOAc and spectroscopic grade MeOH were used without further purification. All the other reagents and solvents used in this study were of guaranteed reagent grade.

Methods

In 10 ml standard flasks, 1 ml of 40 mM 3HF and 0.5 ml of 40 mM AlCl₃ solution were equilibrated for 1 h to ensure complete complexation followed by addition of various F⁻ (or OAc⁻) μM concentrations and made up to the mark with MeOH. After further equilibration of each solution for 1 h at room temperature (25°C) the electronic and fluorescence spectra were recorded. The anion binding ability of Al (3HF)₂ was studied by means of UV-vis and fluorescence titration experiments with MeOH as solvent.

Results and discussion

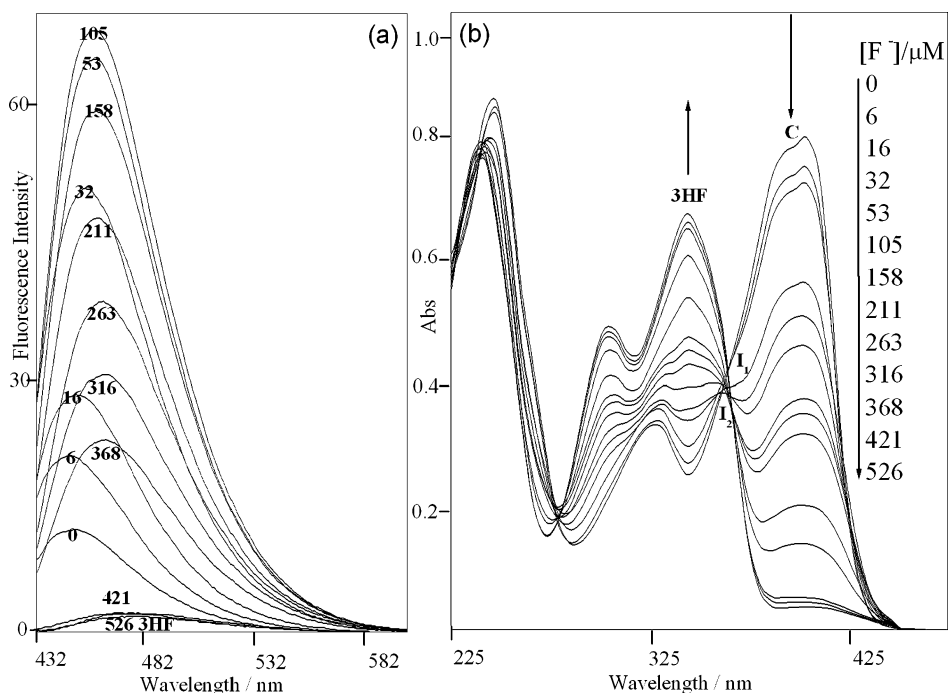
A successive increase in the fluoride ion concentration ranging from 0–526 μM resulted in the decrease in absorbance of the complex peak of the chelate at 402 nm, while the free 3HF peak at 344 nm showed an increase. With F⁻ addition between 0–105 μM, complex (2, Scheme 1), is at equilib-



Scheme 1

rium with intermediate (3) in solution, at the isosbestic point at 362 nm (I₁, Fig. 1) of the absorption spectra. This is accompanied by a simultaneous enhancement in the fluorescence intensity of the complex with a smooth red shift from the emission maxima, 448 nm to 458 nm. For 158–526 μM F⁻, intermediate (3), is at equilibrium with 3HF (1), at the isosbestic point at 366 nm (I₂). A corresponding decrease in the fluorescence intensity of the intermediate with a red shift from 458 nm to 472 nm was observed with the regeneration of 3HF. Fluoride ion detection range from 6 μM to 50 mM is offered by this Al (3HF)₂ complex and the intermediate system by a concerted co-ordination of the fluoride ion [3] having a high affinity to Al(III) [34–36].

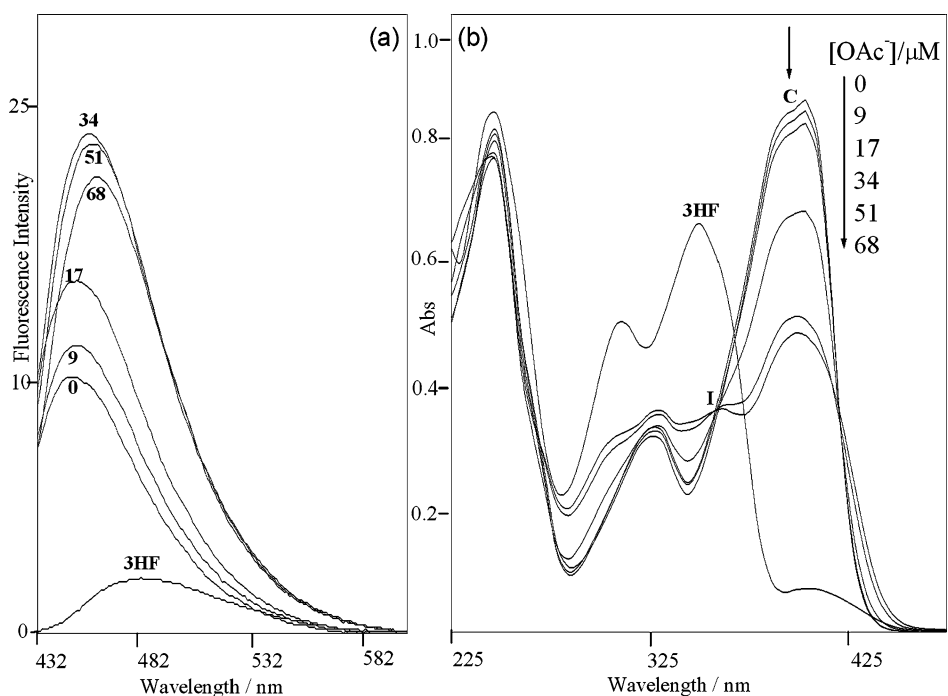
Fig. 1 (a) Change in fluorescence spectra ($\lambda_{\text{ex}} = 402 \text{ nm}$) and (b) UV-vis spectra for 3HF- Al(III) complex (C) upon F addition in MeOH at 25°C



This unusual behavior of fluorescence enhancement followed by subsequent decrease in fluorescence intensity on fluoride addition has been explained in the case of biaryl fluorophore [37], a fluorescent fluoride chemosensor based on conformational restriction and its loss, involving an intermediate complex species. Besides, ferrocenyl-naphthalene dyad [38] yields greater fluorescence upon binding to fluoride, related to its excimer

emission, while for [1,8-bis(phenylureido)naphthalene] [39], it is due to enhanced planarity on in-plane binding. Mixed-ligand complexes of intense fluorescence are formed by Tris(2-methyl-8-quinolinolato)aluminium [40] on binding to HSO_4^- . Based on the details available from this literature and from our extended experimental study, Scheme 1 was adopted as the reaction mechanism.

Fig. 2 (a) Change in fluorescence spectra ($\lambda_{\text{ex}} = 402 \text{ nm}$) and (b) UV-vis spectra for 3HF- Al(III) complex (C) upon OAc addition in MeOH at 25°C



In case of acetate ion addition between 0–68 μM , complex (2), is at equilibrium with intermediate (4) in solution, at the isosbestic point at 360 nm (I, Fig. 2) of the absorption spectra. A corresponding increase in the fluorescence intensity of the complex for 0–34 μM OAc^- is followed by a subsequent decrease for 34–68 μM OAc^- with a continuous red shift from 448 nm to 456 nm. Any further addition of OAc^- , going up to 0.1 M, does not cause a decrease in absorbance of the intermediate peak at 400 nm and induces only a nominal change in fluorescence intensity, similar to the derivative of anthracene carbamate [41], that acts as an acetate sensor. This is a strong indication about the stability of the intermediate (4) and a measure to judge the Al(III) affinity and complexing ability of F^- and oxygen of OAc^- . For, at 526 μM F^- , we have the complete regeneration of 3HF as compared to the presence of intermediate (4), up to 0.1 M OAc^- . The in-situ intermediate (4), was precipitated as (5) out of MeOH solution containing, 4 mM 3HF, 2 mM AlCl_3 and 7 mM OAc^- . The structure of (5) was inferred from the FT-IR spectrum and ESI-MS of the sample.

The confirmation on the presence of acetate groups in the precipitated intermediate (5) was arrived at from studying the IR absorptions ($\nu_{\text{max}}/\text{cm}^{-1}$) of the sample. Acetates produce IR active vibrational modes of 2935 and 2833 (CH_3), 1443 ($\delta\text{sy-CH}_3$) and 1594 (COO) respectively. The carboxylate stretching frequency for the acetate group occurs at 1560 (COO) [42] as compared to 1594 (COO) in the intermediate, a strong indicator of a unidentate acetate ligand [43]. On comparison of the IR spectrum of the intermediate with 3HF, the conclusions arrived at were, the aromatic stretch which appears at 3069 (CH) in 3HF, occurs at 3068 (CH) in the intermediate, confirming that the 3HF moiety is still part of the intermediate. The 3230 (OH) of 3HF is absent in the precipitate, as the intramolecular H-bond is broken on chelation with Al(III) and the $\text{Al}(\text{3HF})_2$ complex is mainly stabilized by the pyronium form [29]. The carbonyl stretch at 1628 (CO) is down shifted to 1615 (CO), as in the intermediate (5), 3HF is still chelated to Al(III) and the 3448 (OH br) of the precipitate is due to the solvent of crystallization, MeOH in this case. Further, the ESI mass spectrum of the precipitated sample, gave a molecular ion peak at an m/z 593, consistent with structure (5) having three solvent of crystallization, methanol molecules. Subsequent and consecutive loss of the solvent of crystallization, methanol molecules, resulted in a peak at m/z 561 and the base peak at m/z 529 respectively.

Interference study

The sensitivity and selectivity of the $\text{Al}(\text{3HF})_2$ complex signaling system is determined by the affinity of this system to F^- (or OAc^-) in presence of competing foreign ions. Common anions like Cl^- , SO_4^{2-} , NO_3^- , I^- and Br^- did not in-

terfere even when the concentration of the ions are increased hundred fold as compared to that of F^- (or OAc^-) μM in methanol. This selectivity [42] may be due to high charge density of F^- and OAc^- as compared to that of the 3HF moiety, which enables them to strong binding and interaction with Al(III) of the $\text{Al}(\text{3HF})_2$ complex in pure methanol.

Conclusions

The complexation reaction between 3HF and AlCl_3 yields a 2:1 stoichiometry composition of the $\text{Al}(\text{3HF})_2$ chelate in MeOH. The ligand exchange reaction of this chelate with fluoride ion, releases both the 3HF molecules with a rapid change in the absorbance and fluorescence intensity involving an intermediate pathway, while only one 3HF moiety is released with that of acetate ion delivering a quantitative estimation route for F^- and OAc^- ions in the concentration range from 6 μM to 50 mM and between 0–68 μM respectively.

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References

- Beer PD, Gale PA (2001) Anion recognition and sensing: the state of the art and future perspectives. *Angew Chem Int Ed* 40(3):486–516
- Gilles DG, Loher RC (1994) Waste generation and minimization in semiconductor industry. *J Environ Eng* 120:72–86
- Takahashi Y, Tanaka DAP, Matsunaga H, Suzuki TM (2002) Fluorometric detection of fluoride ion by ligand exchange reaction with 3-hydroxyflavone coordinated to a zirconium(IV)–EDTA complex. *J Chem Soc Perkin Trans 2*:759–762
- Badugu R, Lakowicz JR, Geddes CD (2005) A wavelength-ratiometric fluoride-sensitive probe based on the quinolinium nucleus and boronic acid moiety. *Sens Actuators, B* 104:103–110
- Miyaji H, Sessler JL (2001) Off-the-shelf colorimetric anion sensors. *Angew Chem Int Ed* 40(1):154–157
- Ion AC, Ion I, Antonisse MMG, Snelink-Rüuel BHM, et al (2001) Characteristics of fluoride-selective electrode with uranyl salophen receptors in aqueous solutions. *Rus J Gen Chem* 71(2):159–161
- Xu XR, Li HB, Gu JD, Paeng KJ (2004) Determination of fluoride in water by reverse-phase high-performance liquid chromatography. *Chromatographia* 59:745–747
- Yamaguchi S, Akiyama S, Tamao K (2001) Colorimetric fluoride ion sensing by boron-containing π -electron systems. *J Am Chem Soc* 123 (46):11372–11375
- Xu S, Chen K, He Tian (2005) A colorimetric and fluorescent chemodosimeter: fluoride ion sensing by an axial-substituted phosphthalocyanine. *J Mater Chem* 15:2676–2680
- Ferris MM, Leonard MA (1991) Solvent extraction of trace amounts of fluoride prior to, mainly, spectrometry—a review: recent advances in the Alizarin Fluorine Blue approach. *Analyst* 116(4):379–385

- Qing ZC, Long CJ, Hong Z, Qin WY, et al (2005) A colorimetric method for fluoride determination in aqueous samples based on the hydroxyl deprotection reaction of a cyanine dye. *Anal Chim Acta* 539 (1–2):311–316
- Suksai C, Tuntulani T (2003) Chromogenic anion sensors. *Chem Soc Rev* 32(4):192–202
- Savage PB, Holmgren SK, Gellman SH (1994) Anion and ion pair complexation by a macrocyclic phosphine oxide disulfide. *J Am Chem Soc* 116(9):4069–4070
- Jose DA, Kumar DK, Ganguly B, Das A (2004) Efficient and simple colorimetric fluoride ion sensor based on receptors having urea and thiourea binding sites. *Org Lett* 6(20):3445–3448
- Cho EJ, Ryu BJ, Lee YJ, Nam KC (2005) Visible colorimetric fluoride ion sensors. *Org Lett* 7(13):2607–2609
- Ghosh T, Maiya BG (2004) Visual sensing of fluoride ions by dipyrrolyl derivatives bearing electron-withdrawing groups. *J Chem Sci* 116(1):17–20
- Badugu R, Lakowicz JR, Geddes CD (2005) Anion sensing using quinolinium based boronic acid probes. *Curr Anal Chem* 1(2):157–170
- Melaimi M, Gabbay FP (2005) A heteronuclear bidentate Lewis acid as a phosphorescent fluoride sensor. *J Am Chem Soc* 127(27):9680–9681
- Valeur B, Leray I (2000) Design principles of fluorescent molecular sensors for cation recognition. *Coord Chem Rev* 205:3–40
- Martinez-Manez R, Sancenon F (2003) Fluorogenic and chromogenic chemosensors and reagents for anions. *Chem Rev* 103(11):4419–4476
- Miyaji H, Collinson R, Prokes I, Tucker JHR (2003) A ditopic ferrocene receptor for anions and cations that functions as a chromogenic molecular switch. *Chem Commun* 64–65
- de Silva AP, McClean GD, Pagliari S (2003) Direct detection of ion pairs by fluorescence enhancement. *Chem Commun* 2010–2011
- Lehaire M L, Scopelliti R, Piotrowski H, Severin K (2002) Selective recognition of fluoride anion using a Li⁺-metallacrown complex. *Angew Chem Int Ed* 41:1419–1422
- Koskela SJM, Fyles TM, James TD (2005) A ditopic fluorescent sensor for potassium fluoride. *Chem Commun* 945–947
- Wiskur SL, Ait-Haddou H, Lavigne JJ, Anslyn EV (2001) Teaching old indicators new tricks. *Acc Chem Res* 34(12):963–972
- Kubo Y, Kobayashi A, Ishida T, Misawaa Y, James TD (2005) Detection of anions using a fluorescent alizarin-phenylboronic acid ensemble. *Chem Commun* 2846–2848
- Kubo Y, Ishida T, Kobayashi A, Misawaa Y, James TD (2005) Fluorescent alizarin-phenylboronic acid ensembles: design of self-organized molecular sensors for metal ions and anions. *J Mater Chem* 2889–2895
- Cornard JP, Merlin JC (2002) Spectroscopic and structural study of complexes of quercetin with Al(III). *J Inorg Biochem* 92:19–27
- Boudet AC, Cornard JP, Merlin JC (2000) Conformational and spectroscopic investigation of 3-hydroxyflavone-aluminum chelates. *Spectrochim Acta, Part A* 56:829–839
- Engelmann MD, Hutcheson R, Cheng IF (2005) Stability of Ferric Complexes with 3-Hydroxyflavone (Flavonol), 5,7-Dihydroxyflavone (Chrysin), and 3',4'-Dihydroxyflavone. *J Agric Food Chem* 53(8):2953–2960
- Dangleterre L, Cornard JP (2005) Interaction of lead (II) chloride with hydroxyflavones in methanol: a spectroscopic study. *Polyhedron* 24:1593–1598
- Cornard JP, Dangleterre L, Lapouge C (2006) DFT and TD-DFT investigation and spectroscopic characterization of the molecular and electronic structure of the Zn(II)-3-hydroxyflavone complex. *Chem Phys Lett* 419:304–308
- Cornard JP, Merlin JC (2001) Structural and spectroscopic investigation of 5-hydroxyflavone and its complex with aluminium. *J Mol Struct* 569:129–138
- Willard HH, Horton CA (1952) Fluorometric Determinations of Traces of Fluoride. *Anal Chem* 24:862–865
- Martin RB (1996) Ternary complexes of Al³⁺ and F⁻ with a third ligand. *Coord Chem Rev* 149:23–32
- Badr IHA, Meyerhoff ME (2005) Fluoride-selective optical sensor based on Aluminum (III)-octaethylporphyrin in thin polymeric film: further characterization & practical application. *Anal Chem* 77(20):6719–6728
- Lee DH, Im JH, Lee JH, Hong JI (2002) A new fluoride chemosensor based on conformational restriction of a biaryl fluorophore. *Tetrahedron Lett* 43:9637–9640
- Zhang BG, Xu J, Zhao YG, Duan CY, Cao X, et al, (2006), Host-guest complexation of a fluorescent and electrochemical chemosensor for fluoride anion. *Dalton Trans* 10:1271–1276
- Xu G, Tarr MA (2004) A novel fluoride sensor based on fluorescence enhancement. *Chem Commun* 1050–1051
- Yuchi A, Hiramatsu H, Ohara M, Ohata N (2003) Performance of Tris (2-methyl-8-quinolinolato) aluminum as fluorescent anionophore. *Anal Sci* 19:1177–1181
- Chen QY, Chen CF (2004) A new fluorescent as well as chromogenic chemosensor for anions based on an anthracene carbamate derivative. *Tetrahedron Lett* 45:6493–6496
- Ibrahim M, Koglin E (2004) Vibrational spectroscopic study of acetate group. *Acta Chim Slov* 51:453–460
- Chidambaram D, Halada GP (2001) Infrared microspectroscopic studies on the pitting of AA2024-T3 induced by acetone degreasing. *Surf Interface Anal* 31:1056–1059