Photochemical & Photobiological Sciences

View Article Online View Journal

An international journal

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: A. Misra, S. Maity, M. Shyamal, R. Maity, N. Mudi, P. Hazra, P. K. Giri, S. S. Samanta and S. Pyne, *Photochem. Photobiol. Sci.*, 2020, DOI: 10.1039/C9PP00472F.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/pps

An Antipyrine based Fluorescent Probe for distinct detection of Pappoo472F Al³⁺ and Zn²⁺ and Its AIEE Behaviour

Samir Maity, Milan Shyamal, Rakesh Maity, Naren Mudi, Paresh Hazra, Prabhat Kr. Giri, Shashanka Shekhar Samanta, Santanu Pyne and Ajay Misra*

Department of Chemistry, Vidyasagar University, Midnapore 721 102, W.B, India.

Corresponding Author:

E-mail: ajay@mail.vidyasagar.ac.in; Tel.: +91 8967986988; Fax: +91 3222 275329

Abstract

A simple antipyrine based fluorescent probe,4-[(2-Hydroxy-3-methoxy-benzylidene)amino]-1,5-dimethyl-2-phenyl-1,2-dihydro-pyrazol-3-one(OVAP)has been successfully synthesized using one step condensation method. It exhibits dual sensing property toward Al³⁺ and Zn²⁺in presence of other relevant metal ions and also displays novel aggregation induced emission enhancement (AIEE) characteristics in its aggregated/solid state. Aggregated OVAP microstructures with interesting morphologies have been synthesized using SDS as morphology directing agent. Morphologies of the particles are characterized using optical microscopy. Photophysical properties of as synthesized OVAP hydrosol are studied using UV–Vis absorption, steady state and time resolved fluorescence spectroscopy. The 'turn on' luminescent property of OVAP is used for the selective detection of trace amounts of Al³⁺ and Zn²⁺and a significant turn on fluorescence enhancement over ~100-fold is triggered via chelation-enhanced fluorescence (CHEF) through complex formation. The 1:1 stoichiometry of the each sensor metal ion complex is observed from Job's plot based on UV-Vis absorption titration. The LODs for Al³⁺and Zn²⁺are found to be 1.05 nM and 2.35 nM, respectively. Notably, the sensor, OVAP is further demonstrated by molecular INHIBIT logic gate.

Keywords: OVAP; AIEE; Morphology; DFT; Dual Sensor; Molecular logic gate

Introduction

View Article Online DOI: 10.1039/C9PP00472F

Organic luminescent materials that show fluorescence in solid state have been paying attention owing to its potential applicationsinfluorescencesensors¹, semiconductorlasers,² optoelectronicdevices³ etc .Luminescent organic aggregates such as amorphous solids, nanocrystals or microcrystals are found to be much more photostable than isolated molecules.⁴On the other hand these aggregates evoke significant interest for their potential applications in sensors, flat panel display and illumination, etc.⁵⁻⁸due to their unique photophysical properties and low cost structural design. Most organic luminescent materials exhibits strong emission in their dilute solution, but their emissions disappeared hastily on increasing concentrations in solution or aggregations in solid state because of strong intermolecular π - π stacking interactions and other non-radiative decay pathways. This phenomenon is popularly known as Aggregation Caused Quenching (ACQ) effect.⁹Some anti-ACQ materials were reported by Tang¹⁰ and Park¹¹.Fluorophores showing aggregation induced emission enhancement(AIEE) characteristics have successfully been utilized in organic light emitting diodes(OLEDs),¹² electroluminescent materials,¹³ photoemitters,¹⁴ mechanochromism,¹⁵ sensors¹⁶⁻²⁰ etc.

In connection with the sensing of biologically and environmentally relevant ions, fluorescence based tools are considered to have enhanced the capabilities for sensing of specific target analytes.^{21,22}A fluorescent probe produces a detectable fluorescent signal upon interaction with a chemical species²³ and a number of mechanisms like photoinduced electron/energy transfer (PET),²⁴chelation-enhanced fluorescence (CHEF),²⁵fluorescence resonance energy transfer (FRET),²⁶metal-ligand charge transfer (MLCT),²⁷excited-state intra/intermolecular proton transfer (ESIPT),²⁸excimer/exciplex formation,²⁹intramolecular charge transfer (ICT),³⁰and C=N isomerisation³¹are being used to explain the chemo sensing processes. Compare to other transition metal ions, selective chemo sensors for Al³⁺are limited due to its poor coordination power and lack of spectroscopic characteristics.³²⁻³⁶ It has been observed that as a hard acid Al³⁺ prefers hard base containing N and O donor atoms.³⁷Consequently, it is highly demanding to develop simply synthesizable fluorescent chemo sensors for selective and rapid recognition of Al³⁺.On the other hand, there has been increasing interest to develop highly selective and sensitive chemo sensor for Zn²⁺among the researchers. Fluorogenic chemo sensor is found to be primary choice for Zn²⁺ detection due to its closed shell configuration (3d¹⁰4s⁰) which does not produce spectroscopic or magnetic signals.^{38,39}Due to the importance of Al³⁺ and Zn²⁺, many fluorescent chemo sensors for

separate detection of Al^{3+} ions and Zn^{2+} ions have been reported. Yet, most of them contractice online potential toxic substance in their ingredients, which will pollute the environment and harm human health. Additionally, many chemo sensors need complicated syntheses involving harsh reaction conditions and expensive chemicals. More significantly, very few fluorescent chemosensory can selectively detect both Al^{3+} and Zn^{2+} simultaneously.⁴⁰⁻⁴⁶So, it is desirable to develop fluorescent chemo sensors with high sensitivity and selectivity for multi-metal ions.

Considering the above fact, we successfully synthesized simple antipyrine based Schiff base 4-[(2-Hydroxy-3-methoxy-benzylidene)-amino]-1,5-dimethyl-2-phenyl-1,2dihydro-pyrazol-3-one (OVAP) with potential hard N, O donor atoms through a simple onestep synthetic process, where free rotating groups antipyrine and hydroxybenzene moieties are attached to the azo group. Schiff base was found to be poorly fluorescent in good solvent, in part due to isomerization through rotation around the C=N double bond in the excited state.⁴⁷But our synthesized OVAP as a fluorescent "turn on" chemo sensor can recognize selectively both Al^{3+} and Zn^{2+} ion via CHEF process. On the other hand, Aggregated OVAP exhibits AIEE effect and strong yellow fluorescence is observed under ultraviolet irradiation. Microstructures of OVA with various morphologies have been synthesized using SDS as morphology directing agent.

Experimental section

Materials

4-aminoantipyrine was purchased from Merck India Ltd. Ortho-Vanillin was purchased from Sigma-Aldrich Chemical Corp. All the solvents used were of analytical grade. Sodium dodecyl sulphate (SDS) was purchased from Merck India Ltd. and was recrystallized from 1:1 ethanol water mixture. Purity of these chemicals was checked spectrophotometrically. Salts(Nitrate and chloride) of all cations (Aldrich and Merck) were of high purity and used without further purification. Triply distilled deionized water was used throughout the experiments.

Synthesis of OVAP and OVAP Microparticles

Ortho-Vanillin (1 equiv) was added to 4-aminoantipyrine(1 equiv) in 50 mL methanol with constant stirring for 5h. The reaction was monitored by thin-layer chromatography. After completion, pale yellow color solid product was filtered, washed thoroughly with methanol, recrystallized and then dried in a desiccators. Yield: 82%. Anal. Calcd for

& Photobiological Sciences Accepted Manuscrip

hotochemical

C₁₉H₁₉N₃O₃: C, 67.64%; H, 5.68%; N, 12.46%; Found: C, 67.28%; H, 5.29%; N, 12.239, FT-IR (KBr), v, cm⁻¹: 3431 (O – H), 1665 (C = 0), 1598 (C = N), 1459, 1411 (C = C), 1296, 1249 (C–O), 1136 (O – H). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 13.92 (H, s (OH)), 9.84 (H, s (–CH=N)), 7.53–6.83 (8H, ArH), 4.00 (OCH3, s), 3.259 (s, 3H), 2.441 (s, 3H); ¹³C NMR (400 MHz, CDCl₃, δ (ppm)) δ : 10.13, 35.59, 56.07,113.60, 116.01, 118.47, 120.16, 123.61, 124.70, 127.35, 129.31, 134.33, 148.10, 149.91, 150.44, 160.24, 160.48 ppm. The ¹H NMR and ¹³C NMR peaks of OVAP are similar to the earlier reported data.^{48,49}

The microstructures of OVAP were prepared by re-precipitation method and SDS was used as morphology directing agent. In a typical preparation, small volume of 1mM OVAP in EtOH was injected into 5 mL of continuously stirred water and aqueous SDS separately at room temperature (25° C). Clearness of the solution was gradually disappeared and a milky yellowish color appeared after gradual increase in concentration of OVAP. The solution was allowed to stand for overnight. Concentration of both OVAP and SDS were varied to synthesize various microstructures of OVAP. During the synthesis of sample-a, b, c, d, e, f, & g concentration of SDS (3.96 mM) was kept constant and the concentration of OVAP (sample-a: 19.6 μ M, sample-b: 38.4 μ M, sample-c: 56.6 μ M, sample-d: 74 μ M, sample-e: 90.9 μ M,sample-f: 122.8 μ M, sample-g: 166.6 μ M,) was varied to study the effect of concentration of OVAP on aggregated microstructures. Similar method was used for the preparation of OVAP micro structures in the absence of SDS and the samples are named as sample-a₁ to g₁ respectively.

Scheme 1: Synthesis of 4-[(2-Hydroxy-3-methoxy-benzylidene)-amino]-1,5-dimethyl-2-phenyl-1,2-dihydro-pyrazol-3-one(OVAP)



Characterization

UV-Vis spectroscopic measurements were carried out in a Shimadzu UV-1800 spectrophotometer with a 1cm quartz cuvette. Hitachi F-7000 Fluorescence Spectrophotometer was used to record the fluorescence spectra. ¹H and ¹³C NMR spectra

were recorded on a Bruker ASCEND spectrometer operating at 400MHz in CDC1 Mar Agicle Online deuterated dimethyl sulfoxide (DMSO-d₆). The Fourier transform infrared (FT-IR) spectra were obtained in the range of 4000–400 cm⁻¹ using KBr pellets in a PerkinElmer Spectrum-Two FTIR spectrometer. Fluorescence lifetimes were obtained by the method of Time Correlated Single-Photon Counting (TCSPC) using Horiba, Delta Flex Modular Fluorescence Lifetime System with diode laser excitation source (372 nm) and the detection wavelength were 525 nm for OVAP hydrosol, 520 nm for OVAP with Al3+ and 535 nm for OVAP with Zn²⁺. Lamp profiles were measured with a band-pass of 3 nm using Ludox as scatterer. The decay parameters were analysed using non-linear iterative fitting procedure based on the Marquardt algorithm.⁵⁰ The quality of fit was assessed over the entire decay, with a plot of weighted residuals and other statistical parameters e.g. the reduced χ^2 ratio.⁵¹The signal was collected at magic angle (54.7°) using a PPD-850, Picosecond Photon Detection Module. Time resolution of the experimental setup was ~80 ps. Scanning electron microscopic study of gold coated dried OVAP hydrosols were done using Carl Zeiss EVO 18 scanning electron microscope. Optical microscopic study were carried out using an NIKON ECLIPSE LV100POL upright microscope with CCD camera (model no. Nikon DS-Fi l), polarizeranalyser assembly and 100W mercury lamp as excitation source for emission study. Particlesize distribution was measured by dynamic light scattering (DLS) experiments on a Malvern Zetasizer NanoZS90 instrument.

Limit of Detection (LOD)

The LOD was calculated on the basis of the fluorescence titration.Standard deviation of the blank measurement was obtained from the plot of fluorescence intensity of OVAP as a function of its increasing concentrations. This procedure was repeated five times to get its average. The slopes (k) of 3σ method for sensing Al³⁺ and Zn²⁺ by OVAP was obtained from the plot of OVAP PL emission intensity as a function of increasing Al³⁺& Zn²⁺ concentrations at 520 nm and 535 nm respectively. The detection limit was calculated using the following equation.⁵²

 $LOD = 3\sigma/k$

Where, σ is the standard deviation of blank measurement, and k is the slope of the calibration curve obtained from linear dynamic plot of fluorescence intensity versus increasing concentration of metal ions.

Fluorescence Quantum Yield

We also measured the fluorescence quantum yield of OVAP, OVAP-Al³⁺ and OV₃₉A³⁺ prod³⁺ Zn²⁺ in ethanol and OVAP aggregates in water using the following equation, where quinine sulphate was used as standard with λ_{ex} =350 nm.

$$\Phi_{\rm s} = \Phi_{\rm r} \left(A_{\rm r} F_{\rm s} / A_{\rm s} F_{\rm r} \right) \left(\eta_{\rm s}^2 / \eta_{\rm r}^2 \right)$$

 A_s and A_r are the absorbance of the sample and reference solutions, respectively, at the same excitation wavelength, F_s and F_r are the corresponding relative integrated fluorescence intensities, η_s and η_r are the refractive index of the sample and reference solutions respectively.

Results and Discussion

Published on 02 April 2020. Downloaded by University of New England on 4/24/2020 8:42:48 AM.

Synthesis of OVAP is depicted in Scheme-1 and synthesis details are described in Experimental Section. It was completely characterized by physicochemical and spectroscopic analysis. Structure and purity of the probe were confirmed using ¹H NMR (Fig.S1) and ¹³C NMR (Fig.S2) spectra. A vibrational band at 1598 cm⁻¹ was observed in the IR spectra (Fig.S3) of OVAP and it is due to the stretching vibrational mode of imine(-CH=N-) group presentin OVAP.

SEM & Optical Microscopic Study

Scanning electron microscopic images of gold coated dried OVAP hydrosol (samplee, f & g) are shown in Fig. 1.Fig. 1 shows rod shaped particles are formed and the length (1-D growth) of the particles increases with increasing concentration of the particles in the samples.



Fig. 1: SEM images of OVAP microstructures prepared in presence of 4 mM SDS (i) samplee (90.0μM OVAP),(ii) sample-f (122.8 μM OVAP) , (iii) sample-g (166.6μM OVAP).

Morphologies of the particles as observed by fluorescence microscopy are shown in Fig.2. At lower concentration of OVAP bar shaped morphologies are clearly observed for the

sample-e, f, g. It shows rod-shaped microstructures with greenish yellow emission upon the online excitation. There is a clear indication that the dimensions of particles increases along its length with increasing concentration of OVAP.



Fig.2: Optical fluorescence microscopy images (under UV excitation) of OVAP microstructure prepared in presence of 4 mM SDS (a) sample-e (90.0 μ M OVAP), (b) sample-f (122.8 μ M OVAP) (c) sample-g (166.6 μ M OVAP).

UV-Vis Study

UV–Vis absorption spectra of OVAP in EtOH and the as prepared hydrosol of OVAP (sample a, b,c,d,e,f,g) are shown in Fig.3.Absorption spectrum of OVAP in EtOH has two distinct regions at 210-280 nm and 300-400 nm respectively. Comparison of UV-Vis spectra of OVAP with that of vanillin and antipyrine moieties in ethanol(Fig.S4) suggests that the structured absorption bands in the region 210-280 nm are due to aromatic π - π * absorption band of O-vanillin and antipyrine group present in OVAP. In order to understand the nature of absorption band at 300-400 nm, we did the UV-Vis absorption study of OVAP and O-vanillin in presence of base (Fig. S5). Gradual increase of base concentration (pH= 8 to 11), a new red shifted broad absorption band ($\lambda_{max} = 390$ nm) for OVAP appear with an isosbestic point at 372 nm (Fig.S5a). Similarly, absorption study of O-vanillin (Fig. S5b), and comparison with OVAP revels that the broad absorption band of OVAP at 300-400 nm is due to intramolecular proton transfer absorption band between phenolic-OH and imine N atom in OVAP.

However, with gradual increase of water fraction, aggregation starts and the absorption maximum at 332 nm diminishes (Fig.3). On the other hand, a new shoulder band at-264 nm is appeared and the absorbance of the band increases with increasing volume percentage of water. In addition, the overall shift of the spectral baseline of samples a-f relative to the

monomer(Fig.S6) is attributed to the scattering of light by the larger aggregated structure online solution.



Fig. 3: UV-Vis absorption spectra of OVAP (47 μ M) in (i) 0% water (OVAP in EtOH), (ii) 20% water, (iii) 40% water, (iii) 60% water, (iv) 80% water, (v) 90% water and (vi) 99% water.

Steady State Emission Study

Published on 02 April 2020. Downloaded by University of New England on 4/24/2020 8:42:48 AM

PL spectra of OVAP in EtOH and its aggregated hydrosol (in 4mM SDS)with different amount of OVAP is shown in Fig.4a. It is observed that the dilute solution (6 μ M) of OVAP in EtOH exhibits very weak broad emission band with peak maximum at 550nm upon photo excitation at 360 nm. But the aggregated hydrosol of OVAP in SDS (4 mM) medium exhibits nearly 25 nm blue shifted intense structured emission with a maximum at 525 nm. It is also observed that the fluorescence intensity of OVAP hydrosol in the region 475-650 nm increases gradually with the increasing concentration of OVAP. This is due to aggregation-induced emission enhancement (AIEE)effect. Energy optimized structure of OVAP (Fig.S7) suggests that the molecule OVAP as a whole is floppy in nature. Now upon aggregation in its aggregated hydrosol, the floppiness of the molecule decreases, resulting the restriction of intramolecular rotation (RIR) to be operative to show AIEE emission. Also a similar observation in PL study using different concentration of OVAP without SDS is shown in Fig. 4b.It shows that the PL intensity of the aggregated hydrosol of OVAP without SDS is

lower compared to the hydrosol in SDS medium but there is a clear signature of ATET^{icle Online} compare to OVAP in EtOH.

Fig.4c shows the fluorescence emission spectra of OVAP at different volume fractions of water for a fixed concentration of OVAP(47 μ M). It is observed that PL intensity increases gradually up to 90% water fraction, indicating the fabulous AIEE properties of OVAP. Buta sharp change of PL spectra with increased intensity are observed as the volume percentage of water changes from 90% to 99%. Fluorescence emission study at different interval of time of OVAP hydrosol shows that it takes nearly 20 minutes to attain stable emission intensity. This is due to the time required to attain thermodynamically stable aggregates of OVAP in 99% volume percentage of water. PL spectrum of the aggregated hydrosol at 99% v/v is blue shifted and it is due to comparatively less polar environment faced by OVAP in its aggregated state. A plot of PL emission intensity as a function of volume fraction of water. Time evolution of emission intensity of OVAP hydrosol in 99% volume fraction of water shows that it takes nearly twenty minutes to attain the maximum stable intensity of hydrosol (Fig. S8). On the other hand, we also measured the solid state emission of OVAP which is similar to that of the aggregated hydrosol of OVAP (Fig.S9).



Fig.4: (a) Fluorescence emission spectra of (i) OVAP in EtOH, and OVAP hydrosol prepared tele Online in the presence of 4 mM SDS (ii) sample-a, (iii) sample-b, (iv) sample-c, (v) sample-d, (vi) sample-e, (vii) sample-f, (viii) sample-g. (b) The Fluorescence emission spectra of (i) OVAP in EtOH and OVAP hydrosol prepared in the absence of SDS (ii) sample-a₁, (iii) sample-b₁, (iv) sample-c₁, (v) sample-d₁, (vi) sample-e₁, (vii) sample-f₁, (viii) sample-g₁. All emission spectra were taken with 360 nm excitation. (c) Emission spectra of freshly prepared OVAP (62 μ M) in 0% - 99% water. λ_{ex} : 360 nm. (d) Plot of relative variation of PL intensity Vs water volume percentage in the EtOH/water mixture. Insets: Fluorescence images of OVAP (0% and 99% H₂O) under the illumination of 366 nm light.

Time-Resolved Photoluminescence (TRPL)Measurements

Published on 02 April 2020. Downloaded by University of New England on 4/24/2020 8:42:48 AM.

In order to understand the Photophysical behaviour of OVAP and its hydrosol, time resolved photo luminescence (TRPL) were carried out as shown in Fig.5. Measurement of fluorescence lifetime is more robust compare to fluorescence intensity, because it depends neither on the excitation photon density nor on the concentration of the fluorophore. Fig.5 shows the fluorescence decay of OVAP in pure EtOH and EtOH-H₂O (99%) mixture. Analysis of fluorescence decay curve shows that the fluorescence lifetime value increases from 96 ps for OVAP in EtOH to 1.72 ns for OVAP aggregates in 99% volume fraction of water. The measured emission quantum yield of OVAP in EtOH and aggregated hydrosol of OVAP are $\Phi_{\text{OVAP}}(\text{EtOH})=0.009$ and Φ_{OVAP} (agg)= 0.172 respectively. On the basis of radiative rate constant (K_r) and emission quantum yield, we have calculated the non- radiative rate constant (K_{nr}) and the values are listed in Table-1. There is almost 21times decreased of K_{nr} value is observed upon aggregation of OVAP. Thus the increased PL lifetime of OVAP aggregates is the results of decreases of non-radiative process due to restrictions of intramolecular rotational(RIR) motion upon aggregation.



Fig.5:Time-resolved fluorescence spectra of OVAP in ethanol (0% water; red), OVAP hydrosol (99% water; blue) and Lamp (black). λ_{ex} = 372 nm and λ_{em} = 550 nm (OVAP in ethanol), λ_{em} = 525 nm (OVAP hydrosol).

DLS Measurement

DLS measurements were also performed in support of average particle size distribution of OVAP aggregates in the presence of 99% water volume fraction in H₂O/EtOH mixture (Fig. S10). DLS studies revealed that the diameter of the aggregated particles lies between 200 nm to 400 nm and the average calculated diameter of OVAP aggregates is found to be \sim 310nm and this is in the range of previously reported many other AIEE systems [21,22].

Analytical Performance: Sensing Knack toward Al³⁺& Zn²⁺ Ions UV-Vis Study of OVAP in the Presence of Metal Ions

Interaction of OVAP with various metal ions (Na⁺, K⁺, Ag⁺, Mg²⁺, Ca²⁺, Co²⁺, Ni²⁺, Cu²⁺, Cd²⁺, Zn²⁺, Pb²⁺, Hg²⁺, Cr³⁺, Fe³⁺, Al³⁺ and Mn²⁺) was performed in EtOH medium. The absorption spectrum of chemo sensor OVAP exhibits two weak absorption bands at 229 nm and 272 nm, a broad band at 334 nm originating due to intramolecular proton transfer absorption of OVAP (Fig.6). The position of absorption band remained unchanged with most of the metal ions (1 equivalents of each)except Al³⁺, Co²⁺, Cu²⁺, Ni²⁺, Cd²⁺, Mn²⁺and Zn²⁺where a broad absorption peak appear at 400-470 nm with a concomitant decreases of 334 nm band. Titration experiments with gradual addition of Al³⁺& Zn⁺²ions resulted in diminishing of the peaks at 229, 272 and 334 nm along with the appearance of a new peak at 406 nm for Al³⁺ and 425 nm for Zn²⁺(Fig.6), and these new peaks are attributed to the strong

View Article Online DOI: 10.1039/C9PP00472F ligand-to-metal charge-transfer (LMCT) absorption band. The presence of isosbestic points article Online 380 and 250 nm established the transformation of a free receptor to its aluminium complex as shown in Fig.6a. Titration experiments with Zn^{2+} also yielded almost similar results as in the case of Al^{3+} (Fig.6b). Interestingly, a colour change from colorless to light yellow and deep yellow was observed with Al^{3+} and Zn^{2+} , respectively (inset Fig.6a and 6b). Job's plot obtained from the titration experiments yielded 1 : 1 stoichiometry of the complex between OVAP and each of metal ions Al^{+3} & Zn^{+2} (Fig. S11a & b) respectively.



Fig. 6:Changes in absorption spectra of OVAP (47 μ M) with (a)increasing concentration (4.9 μ M to 47 μ M) of Al³⁺, (b)increasing concentration (4.9 μ M to 47 μ M) of Zn²⁺.Inset: colour change upon the addition of Al³⁺and Zn²⁺ to OVAP in ethanol.

Fluorescence Study of OVAP in the Presence of Metal Ions

Published on 02 April 2020. Downloaded by University of New England on 4/24/2020 8:42:48 AM.

PL spectra of OVAP in presence of various metal ion in solution are shown in Fig.7.OVAP displays a weak emission peak at 550 nm on excitation at 360 nm. In the presence of various metal ions (Na⁺, K⁺, Ag⁺, Mg²⁺, Ca²⁺, Co²⁺, Ni²⁺, Cu²⁺, Cd²⁺, Zn²⁺, Pb²⁺, Hg²⁺, Cr³⁺, Fe³⁺, Al³⁺, Mn²⁺ in ethanolic solution), a remarkable enhancement of the emission spectra of OVAP was observed only with Al³⁺ and Zn²⁺peaking at two distinct wavelengths, 520 nm and 535 nm, respectively (Fig.7a & 7b). Green fluorescence was observed in the case of Al³⁺ whereas yellowish green fluorescence was observed in presence of Zn²⁺ (inset Fig.7a & 7b). These results also validated the selectivity of OVAP towards Al³⁺ and Zn²⁺. Fluorescence titration experiments were also carried out with gradual addition of Al³⁺ and Zn²⁺ to the solution of OVAP. In both the cases, a gradual increase in emission intensity of OVAP in presence of metal ions (Al³⁺ & Zn²⁺) was observed (Fig.7). Relative fluorescence colour changes of OVAP in presence of Al³⁺ and Zn²⁺ are shown in the inset of Fig.7a & 7b

respectively. Fluorescence titration using the equimolar mixture of Al^{3+} and Zn^{2+}_{DC} (Fig. 3) (Fig



Fig. 7: Fluorescence emission spectra of OVAP (47 μ M) (a) with the increasing concentration (4.9 μ M to 47 μ M) of Al³⁺. [Inset: colour change upon the addition of Al³⁺ to OVAP under UV light irradiation, $\lambda = 366$ nm]. (b) with increasing concentration (4.9 μ M to 47 μ M) of Zn²⁺[Inset: colour change upon the addition of Zn²⁺ to OVAP under UV light irradiation, $\lambda = 366$ nm]. (c) Plot of emission intensity at 520 nm vs. [Al³⁺]. (d) Plot of emission intensity at 535 nm vs. [Zn²⁺]. Excitation wavelength for all the emission spectra is 360 nm.

Time-Resolved Photoluminescence(TRPL)Study

The TRPL measurements were also carried out to better understand the mechanism of the 'turn-on' emission responses of OVAP toward Al^{3+} and Zn^{2+} ion as shown in Fig.8. The fluorescence lifetime (τ) of OVAP in EtOH is 96 ps, whereas longer average fluorescence lifetimes of 2.23 ns and 2.32 ns were detected in the presence of 1:1 equiv of Al^{3+} & Zn^{2+} respectively. Our measured fluorescence quantum yield for OVAP, OVAP-Al^{3+} and

OVAP-Zn²⁺ in EtOH are 0.009, 0.68 and 0.47 respectively (Table-1). We further calculate Online

the non-radiative rate constant of OVAP and its complex with Al³⁺& Zn²⁺ (Table-1). On the basis of the measured fluorescence quantum yield and fluorescence lifetime, the nonradiation rate constant of OVAP in EtOH, OVAP hydrosol, OVAP-Al³⁺ and OVAP-Zn²⁺ were obtained as 10.32, 0.48, 0.14 and 0.22 S⁻¹ respectively. The observed non-radiative rate constant of OVAP is nearly 20,50, and 100 times higher compare to aggregated hydrosol, $OVAP-Zn^{2+}$ and $OVAP-Al^{3+}$ complexes respectively. This higher K_{nr} vale of OVAP is Published on 02 April 2020. Downloaded by University of New England on 4/24/2020 8:42:48 AM



Fig. 8: Time resolved fluorescence spectra of OVAP (47 μ M) in EtOH and OVAP with Al³⁺& Zn²⁺ respectively. Lamp (black), OVAP in EtOH (red), 1:1 equiv OVAP &Al³⁺(blue); 1:1 equiv OVAP & Zn^{2+} (pink); ($\lambda_{ex} = 372$ nm, $\lambda_{em} = 520$ nm for Al³⁺& OVAP and 535 nm for Zn²⁺& OVAP).

				4	
	a	h	Δ_		٠
_	а	υ	ι-	L	٠

View Article Online DOI: 10.1039/C9PP00472F

Sample	$\tau_{ m f}$	$\Phi_{\rm f}$	$K_{\rm r}$ (S ⁻¹)	$K_{\rm nr}$ (S ⁻¹)	χ^2
	(avg. ns)		$(\Phi_{\rm f}/\tau_{\rm f})$	$[(1/\tau_{\rm f}) - K_{\rm r}]$	
OVAP in EtOH	0.096	0.009	0.093	10.32	1.27
Aggregated OVAP (99% H ₂ O)	1.72	0.172	0.1	0.48	1.12
OVAP+Al ³⁺ (1:1) in EtOH	2.23	0.68	0.304	0.14	1.13
OVAP+Zn ²⁺ (1:1) in EtOH	2.32	0.47	0.202	0.22	1.11

Metal Ions Competition Study

The selectivity of OVAP towards Al³⁺ and Zn²⁺ was also established through experiments in the presence of competing metal ions (Fig.9)through UV-Vis and fluorescence emission study. Absorption spectrum of chemo sensor OVAP shows two weak absorption bands at 272 and 334 nm (Fig. 6a). The position of absorption band remained unchanged with most of the metal ions except Al³⁺, Co²⁺, Cu²⁺, Zn²⁺, Ni²⁺, Cd²⁺, Mn²⁺ where a new broad band 400-470 nm is appeared. It is interesting to note that among all the tested metal ions only Al³⁺ and Zn²⁺ rendered significant fluorescence 'turn-on' responses, whereas other relevant competing metal ions has no noteworthy effect in the emission spectra(Fig.9b). In order to establish the specific selectivity of OVAP toward Al³⁺ and Zn²⁺, we also carried out the single and dual metal competitive analysis (Fig.S13& S14). Bar diagram plot for the measurement of selectivity of OVAP for Al³⁺, Zn²⁺ ions in the presence of other competitive metal ions are shown in Fig.10. The photographs of OVAP with different metal ions (under normal light and UV light irradiations) well-verified its sensitivity by strong blue fluorescence as depicted in Fig.11.



Fig. 9: a)UV–Vis absorption spectra of OVAP (47 μ M) in theabsences and presence of different metal ions (45 μ M) at 25°C. b) Fluorescence emission spectra of OVAP (47 μ M) in Ethanol in the presence of different metal ions (45 μ M) such as Na⁺, K⁺, Ag⁺, Mg²⁺, Ca²⁺, Co²⁺, Ni²⁺, Cu²⁺, Cd²⁺, Zn²⁺, Pb²⁺, Hg²⁺, Cr³⁺, Fe³⁺, Al³⁺ andMn²⁺. All the emission spectra were taken with excitation at 360 nm.



Fig. 10: Selectivity of OVAP for Al^{3+} , Zn^{2+} ions in the presence of other competitive metal ions, excitation wavelength 360 nm and emission maxima are 520 nm 535 nm for Al^{3+} and Zn^{2+} respectively.



Fig. 11: Visual color change observed with the addition of different metal ions to OVAP as seen under daylight (upper) and UV light (lower) ($\lambda = 366$ nm).

Dissociation Constant

The dissociation constant (K_d) of the corresponding OVAP compounds with Al^{3+/} Zn²⁺ have been determined by fitting the absorption data as a function of metal ion concentration using the following equation,⁵³

 $I = I_0 + (I_{\rm lim} - I_0)/2C_0 [C_0 + C_{\rm M} + K_d - [(C_0 + C_{\rm M} + K_{\rm d})^2 - 4C_0C_{\rm M}]^{1/2}]$

where I₀ and I are the absorbance of OVAP at 406 nm in the absence and presence of Al³⁺and at 425 nm in the absence and presence of Zn²⁺ respectively; C₀is the total concentration of OVAP, C_M is the concentration of metal ion i.e Al³⁺ or Zn²⁺; I_{lim} is the limiting value of the absorption intensity in the presence of excess metal ion. The evaluated K_d values using absorption spectral studies for Al³⁺ and Zn²⁺ are $(1.07 \pm 0.06) \times 10^{-5}$ M and $(6.16 \pm 0.47) \times$ 10^{-6} M respectively (Fig.S15). K_d values of the corresponding divalent ions with OVAP have also been obtained by the non-linear fitting of corresponding fluorescence intensity at 520 nm for Al³⁺ and 535 nm for Zn²⁺using similar type of equation where fluorescence intensity is used instead of absorption value in the above equation and the values are $(1.06 \pm 0.14) \times 10^{-5}$ M for Al³⁺ and $(2.53 \pm 1.71) \times 10^{-6}$ M for Zn²⁺ respectively(Fig.S16). Our observed K_d values obtained from both absorption and emission data are in excellent agreement and it proves the self consistency of our spectral data.

Detection Limit

Sensitivity of the probe are examined by measuring limit of detection (LOD) for each cation. LOD has been determined by following the 3σ method. The LOD values are 1.05 nM for Al³⁺, 2.35 nM for Zn²⁺(Fig.S17). LOD values are exceptionally low compared to the

others.⁵⁴⁻⁶⁰A comparative study of OVAP and other reported dual Al^{3+} & Zn^{2+} sensor $SP_{PO0472F}$ shown in Table-S1. Study shows that the LOD of OVAP for Al^{3+} & Zn^{2+} is comparable to that reported by Alam et. al.⁶⁰ These data indicate that OVAP is highly sensitive towards Al^{3+} and Zn^{2+} ions.

We also demonstrate the visual detection of Al^{3+} and Zn^{2+} by sharp fluorescence changing response on TLC plate upon UV irradiation. We have prepared fluorescent test strips by dip-coating solution of OVAP in methanol on TLC plate simply followed by drying the test strips under vacuum condition. OVAP absorbed on the test strips, show no colour upon UV illumination at 365 nm. But as we irradiated 365 nm light after adding few drops (30 μ M) of Al³⁺ and Zn²⁺ each, strong yellow luminescence appears from the strip containing OVAP+Al³⁺ and green luminescence appears from OVAP+Zn²⁺ containing strip (Fig. S18). This clearly signifies the solid state detection of Al³⁺ and Zn²⁺ at a very low concentration.

Binding Sites and Reversibility

Published on 02 April 2020. Downloaded by University of New England on 4/24/2020 8:42:48 AM.

Stoichiometry and binding sites of OVAP with Al³⁺& Zn²⁺ were determined by¹H NMR titration experiment (Fig.S19& Fig.S20). Upon addition of 0.5 equiv of Al³⁺, the signal of the -OH proton decreases in intensity and finally disappeared at 1.0 equiv. of Al³⁺. A slight down field shift of ¹H NMR signal of imine proton (HC=N) from 9.68 ppm to 9.69 ppm was observed, which strongly suggests the involvement of heteroatoms (O and N) and their chelation to form the Al³⁺-OVAP complex. On the other hand, addition of 0.5 and 1.0 equiv of Zn^{2+} , the proton of the hydroxyl group at 13.039 ppm decreases in intensity and the imine proton (9.68 ppm) was shifted slightly up-field at 9.67 ppm. These results indicated that the nitrogen atom in the imine group and the oxygen atom in the hydroxyl group might coordinate to Zn²⁺ion.No considerable changes in the position of proton signals on further addition (>1.0 equivalent) of Al^{3+} and Zn^{2+} was observed which supports the 1:1 metal to ligand ratio of the Al³⁺-OVAP & Zn²⁺-OVAP complex and it was further supported by the Job's plot. Again chelation site of metal ions with OVAP was supported by DFT based computational study. It has been shown that the possible location of metal ions at the imine chelation site has the lowest optimized energy structure for both Al³⁺-OVAP & Zn²⁺-OVAP complex (Fig.S21). Bond distances between metal ions (Al³⁺ and Zn²⁺) and the binding sites of OVAP are shown in table-S2. The observed bond distance between the metal ion and atoms in the chelating sites of OVAP as observed from DFT study show that the binding with Al^{3+} is more rigid than Zn^{2+} and it is reflected in the lower k_{nr} values in Al^{3+} -OVAP complex than Zn^{2+} -OVAP complex.

Furthermore, complexation behaviour was well-supported by the reversibility of $\Delta B^{3+tricle Online}$ OVAP and Zn²⁺-OVAP. Reversibility is one of the most important features to convince the demand of a novel chemo sensor mainly for improving practical real time applications of a probe. To examine the reversible binding of OVAP with Al³⁺ and Zn²⁺, we used EDTA as a strong chelating ligand at identical reaction conditions(Fig.12). The fluorescence intensity of OVAP in the presence of Al³⁺(at 520 nm)and Zn²⁺(at 535 nm)decreased immediately when excess EDTA was added due to dechelation of Al³⁺and Zn²⁺from the corresponding complex i.e. the sensor complexes, (Al³⁺-OVAP) and (Zn²⁺-OVAP) was found to be reversible with free metal ions & OVAP. We have checked the reversibility study up to 10th cycle for each metal ions (fig.12) and after the end of 10th cycle we obtained almost same fluorescence intensity as in case of 1st cycle. Thus the probe OVAP has excellent stability for reuse.



Fig. 12: Reversibility cycles of OVAP metal complexes with EDTA.

Molecular Logic Operation

An INHIBIT logic gate is made of particular combination of the logic operation of NOT and AND functions, i.e. out-put signal is inhibited by only one type of input. To demonstrate INHIBIT logical function, one can choose two inputs Al^{3+}/Zn^{2+} (input-1) and EDTA (input-2) and the emission intensity at 520nm/ 535nm as the out-put. The high value of emission intensity (>31at 520nm (Fig.13a)) & (>17at 535nm(Fig.13b)) has been assigned as 1(ON) and the low emission intensity (<17at both 520nm & 535nm) has been assigned as 0 (OFF). We further defined the absence of Al^{3+}/Zn^{2+} and EDTA as '0' and their presence as '1'. The out-put signal corresponding to four different inputs i.e. (0,0), (1,0), (0,1) & (1,1) are shown in the truth table (Fig.13c). It is obvious from the truth table, when only input-1 is

present a significant enhancement of emission intensity at 520nm/535nm takes. Disadje Online indicating the 1 (ON) state. On the other hand, when only input-2 is present the output emission intensity becomes very weak indicating OFF state. Therefore it is necessary to apply NOT gate with input-2. In presence of both inputs the emission intensity again low indicating OFF state as listed in the truth table (Fig.13c). Thus INHIBIT function logic gate(Fig. 13d) can be constructed by the sequential application of these two input and it greatly expands the application of chemo-sensor, OVAP.



Published on 02 April 2020. Downloaded by University of New England on 4/24/2020 8:42:48 AM.

Fig. 13: (a)Fluorescence spectra of OVAP (47 μ M) in the presence of Al³⁺ before and after the treatment with excess EDTA ($\lambda_{ex} = 360 \text{ nm}$), (b) Fluorescence spectra of OVAP (47 μ M) in the presence of Zn²⁺ before and after the treatment with excess EDTA ($\lambda_{ex} = 360 \text{ nm}$), (c) Truth table of logic gate, (d) General representation of an INHIBIT logic gate circuit.

In summary, herein we have reported the synthesis of a simple and low-cost fluorescent probe, 4-[(2-Hydroxy-3-methoxy-benzylidene)-amino]-1,5-dimethyl-2-phenyl-1,2-dihydro-pyrazol-3-one (OVAP) which is weakly emissive in solution state, but exhibits interesting aggregation-induced emission enhancement (AIEE) properties in aggregated/ solid state. Microstructures of OVAP with various morphologies are synthesized using reprecipitation method. Again, the 'turn on' fluorescence of OVAP in presence of AI^{3+} & Zn^{2+} has been utilized for sensing single as well as simultaneous presence of AI^{3+} and Zn^{2+} in aqueous solution with LODs 1.05 nM and 2.35 nM respectively. Due to strong overlap of emission band, it is suggested that the band edge emission intensity can be used to detect AI^{3+} and Zn^{2+} simultaneously present in water sample. Further development of dual metal sensing probe showing negligible overlap of emission upon complexation with metal ions are in progress in our lab. It is further demonstrated that the fluorescence 'turn on' emission of OVAP in presence of AI^{3+}/Zn^{2+} and 'turn off' in presence of EDTA can be utilized to fabricate molecular INHIBIT logic gate.

Supplementary Information (SI) Available

¹H NMR Study, ¹³C NMR Study, FT-IR Study, UV-Vis study, solidstateemission study, Job's plot, Competitive analysis study, Dissociation Constant study, Fluorescence Life Time Table, LOD study, ¹H NMR titration, Comparative table with the previously reported dual sensor.

Acknowledgement

S.M (Award No.: 09/599(0065)/2015-EMR-I), N.M (Award No.: 09/599(0075)/2018-EMR-I), S.S.S (Award No.: 09/599(0084)/2019-EMR-I) thanks CSIR, New Delhi, Indiaand P.H (Ref. No.: 204/(CSIR-UGC NET JUNE 2017), P.K.G (Ref. No.: 228/(CSIR-UGC NET DEC 2017) thank UGC, New Delhi, India for their individual fellowship. Departmental instrumental facilities from DST FIST and UGC SAP programs are gratefully acknowledged. We also acknowledge the help render by USIC,Vidyasagar University for doingoptical microscopic study and both steady state and time resolved fluorescence study.

References

Published on 02 April 2020. Downloaded by University of New England on 4/24/2020 8:42:48 AM

View Article Online DOI: 10.1039/C9PP00472F

1. W. C. Wu, C. Y. Chen, Y. Q. Tian, S. H. Jang, Y. N. Y. Liu, R. R. Hu, B. Z. Tang, Y. T. Lee, C. T. Chen, W. C. Chen and A. K. Y. Jen, Enhancement of Aggregation-Induced Emission in Dye-Encapsulating Polymeric Micelles for Bioimaging, *Adv. Funct. Mater.*, 2010, **29**, 1413-1423.

2. I. D. W. Samuel and G. A. Turnbull,Organic Semiconductor Lasers,*Chem. Rev.*,2007,**107** 1272-1295.

3. J. W. Chung, H. Yang, B. Singh, H. Moon, B. K. An, S. Y. Lee and S. Y. Park, Singlecrystalline organic nanowires with large mobility and strong fluorescence emission: a conductive-AFM and space-charge-limited-current study, *J. Mater. Chem.*,2009,**19**, 5920-5925.

4. Y. N. Hong, J. W. Y. Lam and B. Z. Tang, Aggregation-induced emission: phenomenon, mechanism and applications, *Chem. Commun.*, 2009, **0**,4332–4353.

5. W. Chen, J. O. Bovin, A. G. Joly, S. P. Wang, F. H. Su and G. H. Li, Full-Color Emission from In₂S₃ and In₂S₃:Eu³⁺ Nanoparticles, *J. Phys. Chem. B*,2004,**108**, 11927–11934.

6. A. Hagfeldt and M. Gratzel, Light-Induced Redox Reactions in Nanocrystalline Systems, *Chem. Rev.*, 1995, **95**, 49–68.

7. J. Y. Kim and F. E. Osterloh, ZnO–CdSe Nanoparticle Clusters as Directional Photoemitters with Tunable Wavelength, *J. Am. Chem. Soc.*, 2005, **127**, 10152–10153.

8. A. N. Shipway, E. Katz and I. Willner, Nanoparticle arrays on surfaces for electronic, optical, and sensor applications, *Chem Phys Chem*, 2000,1,18–52.

9. S. W. Thomas, G. D. Joly and T.M. Swager, Chemical Sensors Based on Amplifying Fluorescent Conjugated Polymers, *Chem. Rev.*, 2007,107, 1339-1386.

10. J. D. Luo, Z. L. Xie, J. W. Y. Lam, L. Cheng, H. Y. Chen, C. F. Qiu, H. S. Kwok, X. W. Zhan, Y. Q. Liu, D. B. Zhu, B. Z. Tang, Aggregation-induced emission of 1-methyl-1,2,3,4,5-pentaphenylsilole, *Chem. Commun.*, 2001, **0**, 1740-1741.

11. B. K. An, S. K. Kwon, S. D. Jung, S. Y. Park, Enhanced Emission and Its Switching in Fluorescent Organic Nanoparticles, *J. Am. Chem. Soc.*, 2002,**124**, 14410.

12. G. Li, Y. Zhao, J. Li, J. Cao, J. Zhu, X.W. Sun, Q. Zhang, Synthesis, Characterization, Physical Properties, and OLED Application of Single BN-Fused Perylene Diimide, *J. Org. Chem.*, 2015, **80**, 196–203.

13. G. Qian, B. Dai, M. Luo, D. Yu, J. Zhan, Z. Zhang, D. Ma, Z.Y. Wang, Band Gap Tunable, Donor-Acceptor-Donor Charge-Transfer Heteroquinoid-Based Chromophores:

14. A. Hagfeldtt, M. Gratzel, Light-Induced Redox Reactions in Nanocrystalline Systems, *Chem. Rev.*, 1995, **95**, 49–68.

15. Z. Chen, J. Zhang, M. Song, J. Yin, G. A. Yu and S. H. Liu, A novel fluorene-based aggregation-induced emission (AIE)-active gold(i) complex with crystallization-induced emission enhancement (CIEE) and reversible mechanochromism characteristics, *Chem. Commun.*, 2015, **51**, 326-329.

16. S. Maity, M. Shyamal, D. Das, A. Maity, S. Dey, A. Misra, Proton triggered emission and selective sensing of 2,4,6-trinitrophenol using a fluorescent hydrosol of 2-phenylquinoline, *New J. Chem.*, 2018, **42**, 1879–1891.

17. M. Shyamal, P. Mazumdar, S. Maity, S. Samanta, G.P. Sahoo, A. Misra, Highly Selective Turn-On Fluorogenic Chemosensor for Robust Quantification of Zn(II) Based on Aggregation Induced Emission Enhancement Feature, *ACS Sens.*, 2016,1,739–747.

18. M Shyamal, P Mazumdar, S Maity, GP Sahoo, G Salgado-Moran and, A Misra, Pyrene Scaffold as Real-Time Fluorescent Turn-on Chemosensor for Selective Detection of Trace-Level Al(III) and Its Aggregation-Induced Emission Enhancement, *J. Phys. Chem. A*,2016,**120**, 210-220.

19. A. Tang, Z. Chen, D. Deng, G. Liu, Y. Tu, S. Pu,Aggregation-induced emission enhancement (AIEE)-active tetraphenylethene (TPE)-based chemosensor for Hg^{2+} with solvatochromism and cell imaging characteristics,*RSC Adv.*, 2019,9, 11865-11869.

20. A. Tang, Y. Yin, Z. Chen, C. Fan, G. Liu, S. Pu,A multifunctional aggregation-induced emission (AIE)-active fluorescent chemosensor for detection of Zn^{2+} and Hg^{2+} , *Tetrahedron*,2019, **75**, 130489.

A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher, T. E. Rice, Signaling Recognition Events with Fluorescent Sensors and Switches, *Chem. Rev.*,1997,97,1515–1566.

22. G. Aragay, J. Pons, A. Merkoc, Recent Trends in Macro-, Micro-, and Nanomaterial-Based Tools and Strategies for Heavy-Metal Detection, *Chem. Rev.*,2011,**111**,3433–3458.

23. B.Valeur, Molecular Fluorescence Principles and Applications, Wiley-VCH Verlag GmbH, New York, 2001, p. 341.

24. R. Alam, T. Mistri, P. Mondal, D. Das, S. K. Mandal, A. R. Khuda-Bukhsh, M. Ali, A novel copper(ii) complex as a nitric oxide turn-on fluorosensor: intracellular applications and DFT calculation, *Dalton Trans.*,2014,**43**,2566.

25. M. Mameli, M. C. Aragoni, M. Arca, C. Caltagirone, F. Demartin, G. Farruggia, Gewärde Online Filippo, F. A. Devillanova, A. Garau, F. Isaia, A Selective, Nontoxic, OFF–ON Fluorescent Molecular Sensor Based on 8-Hydroxyquinoline for Probing Cd²⁺ in Living Cells, *Chem. Eur. J.*,2010,16,919–930.

26. H.Ueyama, M. Takagi, S. Takenaka, A Novel Potassium Sensing in Aqueous Media with a Synthetic Oligonucleotide Derivative. Fluorescence Resonance Energy Transfer Associated with Guanine Quartet–Potassium Ion Complex Formation, *J. Am. Chem. Soc.*,2002,**124**,14286–14287.

27. P. D. Beer, Transition-Metal Receptor Systems for the Selective Recognition and Sensing of Anionic Guest Species, *Acc. Chem. Res.*,1998,**31**,71.

28. X. Zhang, L. Guo, F. Y. Wu, Y. B. Jiang, Development of Fluorescent Sensing of Anions under Excited-State Intermolecular Proton Transfer Signaling Mechanism, *Org. Lett.*,2003,**5**,2667.

29. B. Schazmann, N. Alhashimy, D. Diamond, Chloride Selective Calix[4]arene Optical Sensor Combining Urea Functionality with Pyrene Excimer Transduction, *J. Am. Chem. Soc.*,2006,**128**,8607.

Published on 02 April 2020. Downloaded by University of New England on 4/24/2020 8:42:48 AM

30. Z. Xu, Y. Xiao, X. Qian, J. Cui, D. Cui, Ratiometric and Selective Fluorescent Sensor for CuII Based on Internal Charge Transfer (ICT), *Org. Lett.*,2005,7,889.

31. J. S. Wu, W. M. Liu, X. Q. Zhuang, F. Wang, P. F. Wang, S. L. Tao, X. H. Zhang, S. K. Wu, S. T. Lee, Fluorescence Turn On of Coumarin Derivatives by Metal Cations: A New Signaling Mechanism Based on C=N Isomerization, *Org. Lett.*,2007,**9**, 33–36.

32. S. H. Kim, H. S. Choi, J. Kim, S. J. Lee, D. T. Quang, J. S. Kim, Novel Optical/Electrochemical Selective 1,2,3-Triazole Ring-Appended Chemosensor for the Al3+ Ion, *Org. Lett.*,2010,**12**,560–563.

33. W. H. Ding, W. Cao, X. J. Zheng, D. C. Fang, W. T. Wong, L. P. Jin, A Highly Selective Fluorescent Chemosensor for Al^{III} Ion and Fluorescent Species Formed in the Solution, *Inorg. Chem.*, 2013, **52**, 7320–7322.

34. S. Sen, T. Mukherjee, B. Chattopadhyay, A. Moirangthem, A. Basu, J. Marek, P. Chattopadhyay, A water soluble Al3+ selective colorimetric and fluorescent turn-on chemosensor and its application in living cell imaging, *Analyst*, 2012, **137**, 3975–3981.

35. L. Wang, W. Qin, X. Tang, W. Dou, W. Liu, Q. Teng, X. Yao, A selective, cell-permeable fluorescent probe for Al3+ in living cells, *Org. Biomol. Chem.*,2010,8,3751–3757.
36. A. Banerjee, A. Sahana, S. Das, S. Lohar, S. Guha, B. Sarkar, S. K. Mukhopadhyay, A. K. Mukherjee, D. Das, A naphthalene exciplex based Al³⁺ selective on-type fluorescent probe

for living cells at the physiological pH range: experimental and computational study of pp00472F *Analyst*, 2012, **137**, 2166–2175.

37. W. H. Ding, W. Cao, X. J. Zheng, D. C. Fang, W. T. Wong, L. P. Jin, A Highly Selective Fluorescent Chemosensor for Al^{III} Ion and Fluorescent Species Formed in the Solution, *Inorg. Chem.*, 2013, **52**, 7320–7322.

38. Z.C. Xu, J. Yoon, D.R. Spring, Fluorescent chemosensors for Zn²⁺, *Chem. Soc. Rev.*,2010,**39**,1996–2006.

39. E. Kimura, T. Koike, Recent development of zinc-fluorophores, *Chem. Soc. Rev.*, 1998, **27**, 179–184.

40. D. Maity, T. Govindaraju, A differentially selective sensor with fluorescence turn-on response to Zn^{2+} and dual-mode ratiometric response to Al^{3+} in aqueous media, *Chem. Commun.*,2012,48,1039–1041.

41. M. Shellaiah, Y. H. Wu, H. C. Lin, Simple pyridyl-salicylimine-based fluorescence "turnon" sensors for distinct detections of Zn^{2+} , Al^{3+} and OH^{-} ions in mixed aqueous media, *Analyst*,2013,**138**,2931–2942.

42. Z. Wang, S. Cui, S. Qiu, S. Pu, A dual-functional fluorescent sensor based on diarylethene for Zn^{2+} and Al^{3+} in different solvents, *J. Photochem. Photobio. A Chemistry*, 2019, **376**,185-195.

43. S. Erdemir, O. Kocyigit, Dual recognition of Zn2+ and Al3+ ions by a novel probe containing two fluorophore through different signaling mechanisms, *Sens. Actua. B Chem.*, 2018, **273**, 56-61.

44. A. Hazra, A. Roy, A. Mukherjee, G. P. Maiti, P. Roy, Remarkable difference in Al³⁺ and Zn²⁺ sensing properties of quinoline based isomers,*Dalton Trans.*,2018,**47**, 13972-13989.

45. A. Roy, U. Shee, A. Mukherjee, S. K. Mandal, P. Roy, Rhodamine-Based Dual Chemosensor for Al^{3+} and Zn^{2+} Ions with Distinctly Separated Excitation and Emission Wavelengths, *ACS Omega*, 2019, **4**, 6864–6875.

46. S. Dey, A. Maity, M. Shyamal, D. Das, S. Maity, P. K. Giri, N. Mudi, S. S. Samanta, P. Hazraa, A. Misra, An antipyrine based fluorescence "turn-on" dual sensor for Zn²⁺ and Al³⁺ and its selective fluorescence "turn-off" sensing towards 2,4,6-trinitrophenol (TNP) in the aggregated state *Photochem. Photobiol. Sci.*, 2019,**18**, 2717-2729.

47. J. S. Wu, W. M. Liu, X. Q. Zhuang, F. Wang, P. F. Wang, S. L. Tao, X. H. Zhang, S. K. Wu, S. T. Lee, Fluorescence Turn On of Coumarin Derivatives by Metal Cations: A New Signaling Mechanism Based on C=N Isomerization, *Org. Lett.*, 2007, **9**, 33–36.

48. B. Anupama, M. Sunita, D. Shiva Leela, B. Ushaiah and C. Gyana Kumari_{DO}Synthese Article Online Spectral Characterization, DNA Binding Studies and Antimicrobial Activity of Co(II), Ni(II), Zn(II), Fe(III) and VO(IV) Complexes with 4-Aminoantipyrine Schiff Base of Ortho-Vanillin, *J. Fluoresc.*, 2014, **24**, 1067-1076.

49. S.Sigroha, B. Narasimhan, P. Kumar, A. Khatkar, K. Ramasamy, V. Mani, R. K. Mishra, A. B. A. Majeed, Design, synthesis, antimicrobial, anticancer evaluation, and QSAR studies of 4-(substituted benzylidene-amino)-1,5-dimethyl-2-phenyl-1,2-dihydropyrazol-3-ones, *Med. Chem. Res.*,2012,**21**,3863–3875.

50. P.R. Bevington, Data Reduction and Error Analysis for the Physical Sciences,McGraw Hill, New York, 1969, pp. 235–237.

51. FELIX 32 Operation Manual, Version 1.1, Photon Technology International, Inc., Birmingham, NJ, 2003.

52. L. Wang, W. Qin, X. Tang, W. Dou, W. Liu, Q. Teng, X. Yao, A selective, cellpermeable fluorescent probe for Al³⁺ in living cells, *Org. Biomol. Chem.*,2010,**8**,3751–3757.

53. M. Maeder, A. D. Zuberbuehler, Nonlinear least-squares fitting of multivariate absorption data, *Anal. Chem.*, 1990, **62**, 2220-2224.

Published on 02 April 2020. Downloaded by University of New England on 4/24/2020 8:42:48 AM

54. Y. S. Kim, G. J. Park, J. J. Lee, S. Y. Lee, S. Y. Lee, C. Kim, Multiple target chemosensor: a fluorescent sensor for Zn(II) and Al(III) and a chromogenic sensor for Fe(II) and Fe(III), *RSC Adv.*,2015,5,11229-11239.

55. S. Goswami, S. Paul, A. Manna, A differentially selective chemosensor for a ratiometric response to Zn2+ and Al3+ in aqueous media with applications for molecular switches, *RSC Adv.*, 2013, **3**, 25079-25085.

56. W. H. Ding, W. Cao, X. J. Zheng, W. J. Ding, J. P. Qiao, L. P. Jin, A tetrazole-based fluorescence "turn-on" sensor for Al(III) and Zn(II) ions and its application in bioimaging, *Dalton Trans.*, 2014, **43**, 6429-6435.

57. Y. Fu, Y. Tu, C. Fan, C. Zheng, G. Liu, S. Pu, A highly sensitive fluorescent sensor for Al³⁺ and Zn²⁺ based on a diarylethene salicylhydrazide Schiff base derivative and its bioimaging in live cells, *New J. Chem.*,2016,**40**,8579-8586.

58. J. Sun, Z. Liu, Y. Wang, S. Xiao, M. Pei, X. Zhao, G. Zhang, A fluorescence chemosensor based on imidazo[1,2-a]quinoline for Al^{3+} and Zn^{2+} in respective solutions, *RSC Adv.*,2015,**5**,100873-100878.

59. J. Qin, L. Fan, B. Wang, Z. Yang, T. Li, The design of a simple fluorescent chemosensor for Al³⁺/Zn²⁺via two different approaches, *Anal. Methods*,2015,7,716-722.

60. R. Alam, T. Mistri, R. Bhowmick, A. Katarkar, K. Chaudhuri, M. Ali, ESIPT blocked CHERPHOLATER based differential dual sensor for Zn^{2+} and Al^{3+} in a pseudo-aqueous medium with intracellular bioimaging applications and computational studies, *RSC Adv.*, 2016, **6**, 1268-1278.

Graphical Abstract

