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A new fluorescent probe for sensing Al³⁺ ions in the solution phase and CH₃COO⁻ in the solid state with aggregation induced emission (AIE) activity†

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An AIE (aggregation induced emission) active probe DFP-AMQ was designed and synthesized as a hexa-coordinated N₂O donor chelator for the selective sensing of Al³⁺ colorimetrically as well as fluorimetrically with a 27-fold fluorescence enhancement for CH₃CN-H₂O (9:1, v/v, pH 7.2, HEPES buffer). The fluorescence enhancement occurred through the blocking of ESIPT, chelation enhanced fluorescence effect (CHEF) arose, and as a result fluorescence enhancement was observed through 1:1 complexation with Al³⁺ ions. Detailed spectroscopic studies including UV-Vis, FTIR, ¹H NMR, and HRMS studies were carried out to characterize the probable structure of DFP-AMQ including the complexation of DFP-AMQ with Al³⁺ ions. The spectrophotometric and spectrofluorimetric titrations revealed strong binding towards Al³⁺ and the *K*_d values were obtained from UV-Vis (3.26 × 10⁻⁵ M⁻¹) and fluorescence titration (2.02 × 10⁻⁵ M⁻¹). The limit of detection of Al³⁺ by DFP-AMQ was 1.11 μM. The quantum yields of DFP-AMQ and [DFP-AMQ-Al]⁺ were calculated to be 0.008 and 0.211, respectively. Dynamic light scattering (DLS) studies showed that the sizes of the particles increased with increasing water percentage due to aggregation. SEM (scanning electron microscopy) studies revealed interesting morphological changes in microstructures in which DFP-AMQ demonstrated a rod-like shape, which was converted to a spherical-like shape in the presence of Al³⁺ and when DFP-AMQ aggregated in H₂O it showed aggregated block-like shape. In the solid phase, DFP-AMQ with nitrate has no particular shape, but in the presence of acetate, it converts to stone-like shape. This probe (DFP-AMQ) could be employed for on-site Al³⁺ ion detection in the solid state.

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1. Introduction

Currently, for the detection of very low levels of molecules/ions, the development of fluorescent sensors has great importance, and in the appraisal of targetable species over fluorescent sensors in solution or in the solid state, several photophysical processes such as CHEF, PET, FRET, and ICT have been considered enormously.¹⁻⁵ Many chemosensors present in the solution state compared to the fluorescent materials in solid states have been reported in the literature. Furthermore in the development of chemical as well as biological sensors due to wide-ranging applications, solid-state fluorescent materials have generated extensive interest ranging from the biomedical to optoelectronic fields in almost all phases of human life.⁶⁻¹⁰ Aggregation induced emission (AIE), used for the development of efficient fluorescent materials in the solid state is a distinctive photophysical phenomenon, which was first observed in the year 2001 in luminogen aggregation, demonstrating intense

emission.¹¹⁻¹³ Furthermore, for the development of fluorescent materials, aggregation induced emission (AIE) has opened a new area. Organic photo-luminescent probes show high fluorescence emissions through aggregation induced emission (AIE) such that the resulting material can bind with molecules *via* strong interaction. The AIE phenomenon occurs from the non-radiative decay when the aggregate state blocks through the control of intra-molecular motions. Likewise, the π-π interactions are prevented by the non-planar conformations, and AIE molecules are fixed when incorporated into solid matrixes, demonstrating strong emission. These special applications make AIE a good candidate for constructing fluorescent materials.¹⁴⁻¹⁷ In dilute solutions, AIE-active sensors show very weak emission and with gradually increasing water percentage, their emission increases because of constrained vibration and rotation.

Aluminium (Al) is the 3rd most abundant element, which plays crucial roles in extensive range of applications including cooking utensils, cosmetics, and potable water supplies.^{18,19} Al³⁺ come into the body through the ecosystem and associate with increased incidences that could be responsible for neurotoxicity causing Alzheimer's and Parkinson's diseases, gastrointestinal and colic problems, bone deformation, anaemia, interruption

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in reproduction, and lung and breast cancer; furthermore, to some extent, certain amount of aluminium is also deadly to plants, fishes, and other living species.^{20–24} As such, for these reasons, there is a social as well as biological significance of Al^{3+} ions, and it is very much important to monitor trace levels of Al^{3+} ions. But it is very difficult to find a technique to sense the aluminium ions as it is not in coloured form. Hence, special attention is necessary to develop a chemosensor for aluminium, though strong hydration of Al^{3+} ions with interfering ions and weak coordination is problematic behaviour. Considering these facts, there are several fluorescent sensors for Al^{3+} ions in the solution state based on different photophysical processes.^{25–30} However, there are very few probes for the detection of Al^{3+} ions based on the AIE effect.^{31,32}

Here we report diformyl phenol and quinoline-based probe **DFP-AMQ**, which is a fluorescent sensor selective on Al^{3+} in the organo-aqueous medium (9 : 1, $\text{CH}_3\text{CN}:\text{H}_2\text{O}$, v/v, in HEPES buffer). Through blocking of ESIPT, chelation-enhanced fluorescence effect (CHEF) occurs and as a result, the fluorescence enhancement was observed. Aggregation induced emission enhancement (AIEE) is active in the presence of water. Dynamic light scattering (DLS) studies show the sizes of the particles, which increase with increasing water percentage due to aggregation. In the solid phase, **DFP-AMQ** shows strong fluorescence but in the presence of nitrate anion, fluorescence emission decreases and again fluorescence emission increased selectively under the presence of acetate anions. Scanning electron microscopy (SEM) shows different microstructures in different conditions. Fluorescence microscope images show the different morphologies in different water percentages.

2. Experimental section

2.1 Materials and methods

The initial materials such as 2,6-diformyl phenol (**DFP**, prepared in the laboratory), 6-amino-2-methyl quinoline (**AMQ**) (Sigma Aldrich), were used to develop the ligand **DFP-AMQ** and to prepare Al^{3+} complexes, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Merck, India) was used. Solvents such as CH_3CN , CH_3OH , and dimethyl formamide (DMF) (Merck, India) were of the reagent grade.

2.2 Physical measurements

PerkinElmer 240 elemental analyzer was used for elemental analysis. Infrared spectra ($400\text{--}4000\text{ cm}^{-1}$) were recorded using KBr pellets on a Nicolet Magna IR 750 series-II FTIR spectrophotometer. A Bruker 300 MHz NMR spectrometer was used for $^1\text{H-NMR}$ recorded in the DMSO-d_6 solvent and using tetramethylsilane ($\delta = 0$) as an internal standard. An Agilent diode-array spectrophotometer (model, Agilent 8453) was used for recording UV-Vis spectra, a Hitachi-7000 spectrofluorimeter was used for recording steady-state fluorescence, ESI- MS^+ (m/z) of the ligand and Al(III) -complex were recorded on a Waters' HRMS spectrometer (model: XEVOG2 QTOF). To analyse the morphology of **DFP-AMQ** in the solid state, FESEM images were taken using an EVO LS10 scanning electron microscope (SEM). For the pH study, a systronics digital pH meter (model 335) was

used and 50 mM HCl or NaOH solution was used for the adjustment of pH. The particle size distribution was measured by dynamic light scattering (DLS) on a Malvern Zetasizer Nano ZS90 instrument. Optical fluorescence microscopy images were taken using a LEICA DM1000 LED upright microscope.

2.3 Preparation of DFP-AMQ

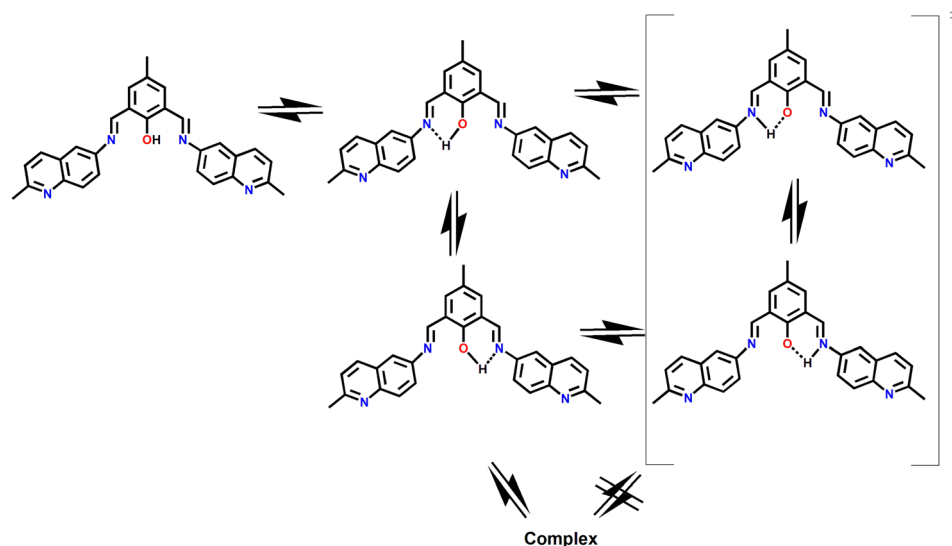
2,6-Diformyl phenol (**DFP**) was prepared by following a literature procedure.³³ 2,6-Diformyl-phenol (**DFP**) (0.82 g, 5 mmol) was dissolved in 15 ml EtOH. To this solution, 6-amino-2-methylquinoline (1.58 g, 10 mmol) was added and the solution was refluxed for 5 h. After that, the reaction mixture was filtered and the filtrate was kept at room temperature. After 2 days a red colour crystalline product was formed (yield, 85.57%). $^1\text{H-NMR}$ (in DMSO-d_6) (δ , ppm): 2.50 (s, 3H, methyl), 2.66 (s, 6H, methyl), 7.44 (s, 2H, aromatic), 7.80 (m, 2H, aromatic), 7.84 (m, 4H, aromatic), 7.99 (d, 2H, aromatic), 8.24 (d, 2H, aromatic), 14.21 (s, 1H, OH) (please see Fig. S1[†]). ESI- MS^+ (m/z): 445.26 (**DFP-AMQ** + H^+) [Fig. S2[†]]. FTIR: 1626 cm^{-1} ($\text{CH}=\text{N}$) [Fig. S3[†]]. Melting point: $98 \pm 1\text{ }^\circ\text{C}$. Elemental analysis: expected: C, 78.36%; H, 5.44%; N, 12.60%; calculated: C, 78.31%; H, 5.37%; N, 12.52%.

2.4 Synthesis of [DFP-AMQ-Al]⁺

DFP-AMQ (0.444 g, 1 mmol, was dissolved in a few drops of DMF), then, 25 ml CH_3CN was added to $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.375 g, 1 mmol in 5 ml MeOH solution) dropwise with continuous stirring. After 1.5 hours, the solution was filtered off and the filtrate was kept aside undisturbed. After one day, $[(\text{DFP-AMQ})\text{Al}]^+$ was crystallised. It was collected by filtration, washed several times with MeCN, and dried in air. Several trials to grow single crystals failed. $^1\text{H-NMR}$ (in DMSO-d_6) (δ , ppm): 2.50 (s, 3H, methyl), 2.67 (s, 3H, methyl), 2.83 (s, 3H, methyl), 7.48–8.30 (12H, aromatic), 9.10 (s, 1H, $\text{CH}=\text{N}$), 9.20 (s, 1H, $\text{CH}=\text{N}$) (Fig. S4[†]). ESI- MS^+ (m/z): 568.52 [$\text{Al}(\text{DFP-AMQ})(\text{H}_2\text{O})_2]^+$, 596.55 [$\text{Al}(\text{DFP-AMQ})(\text{CH}_3\text{OH})_2]^+$ (Fig. S5[†]). FTIR: 1613 cm^{-1} ($\text{CH}=\text{N}$) [Fig. S6[†]].

2.5 Solution preparation for UV-Vis and fluorescence studies

A stock solution of **DFP-AMQ** was prepared ($1.0 \times 10^{-3}\text{ M}$) by dissolving the **DFP-AMQ** in 10 ml CH_3CN for both UV-visible and fluorescence emission titrations. Similarly, another stock solution of Al^{3+} , $1.0 \times 10^{-3}\text{ M}$ was prepared in de-ionised water. 10 mM HEPES buffer (9 : 1 $\text{CH}_3\text{CN}:\text{H}_2\text{O}$) was prepared and the solution of pH was adjusted to 7.2 by using HCl and NaOH. 2.5 ml of the prepared buffer solution was pipetted out into a 5 ml cuvette to which 20 μM of the probe was added and Al^{3+} ion was added gradually starting from 0 to 30 μM in a regular interval of volume and UV-visible and fluorescence emission spectra were recorded for each solution. Path lengths of the cells used for absorption and emission studies were 1 cm. Fluorescence measurements were performed using a 5 nm \times 5 nm slit width.



Scheme 2 The probable pathway for ESIPT.

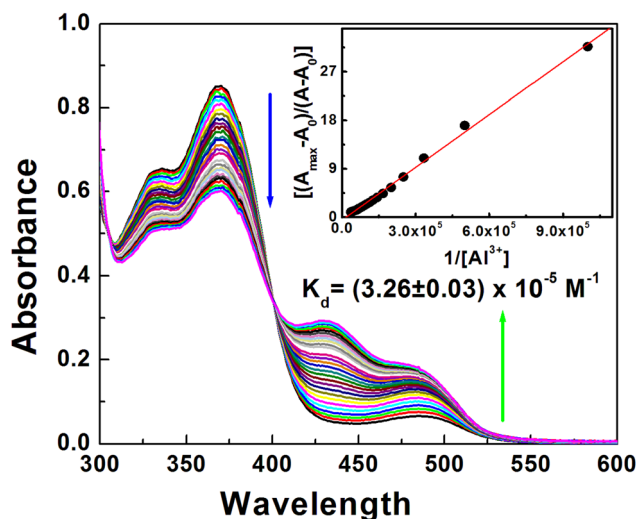


Fig. 1 Absorption titration of DFP-AMQ (20 μM) with Al^{3+} (0–30 μM) in $\text{CH}_3\text{CN-H}_2\text{O}$ (9 : 1, v/v, pH 7.20, 10 mM HEPES buffer). Inset shows Benesi-Hildebrand fitting of the data.

absorption spectra at 369 nm and increase at 432 and 486 nm) obviously indicates that the addition of Al^{3+} ions induces the decrease in the concentration of free ligands both in keto and enol forms. Here, the nitrogen atom takes part in the coordination with Al^{3+} and the formation of the complex inhibits the ESIPT (Scheme 2). UV-Vis absorption studies were performed to investigate the cation binding affinities towards aluminium ions, and when a change in the absorbance at 432 and 486 nm was plotted against $[\text{Al}^{3+}]$, with increasing $[\text{Al}^{3+}]$ a gradual increase in the absorbance was observed.

A linear form of the Benesi-Hildebrand equation (eqn (1)) was used to obtain the dissociation constant and stoichiometry of the complexation, where, A_0 and A_{max} are the absorbances of the ligand in the absence and in the presence of excess metal

ions, respectively, and n is the stoichiometry ($\text{DFP-AMQ} : \text{Al}^{3+}$) of the reaction. A linear least square-fit of $(A_{\text{max}} - A_0)/(A - A_0)$ against $1/[\text{M}]$ clearly demonstrates a 1 : 1 stoichiometry of the reaction ($n = 1$), which also gives an apparent dissociation constants $K_{\text{d}} = (3.26 \pm 0.03) \times 10^{-5} \text{ M}$.

$$\frac{A_{\text{max}} - A}{A - A_0} = 1 + \frac{1}{K_{\text{d}}[\text{M}]^n} \quad (1)$$

3.3 Fluorescence emission studies

The fluorescence emission spectra of DFP-AMQ and its titration with Al^{3+} were recorded in $\text{CH}_3\text{CN-H}_2\text{O}$ (9 : 1, v/v, pH 7.20, HEPES buffer) (Fig. 2) at $\lambda_{\text{ex}} = 400 \text{ nm}$. The binding between the

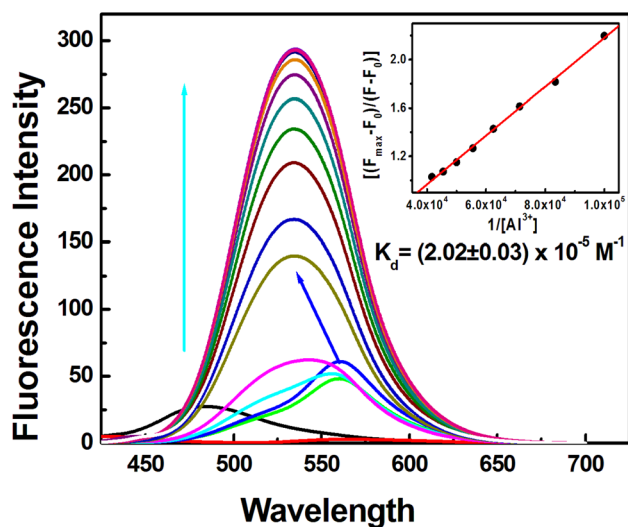


Fig. 2 Fluorescence titration of DFP-AMQ (20 μM) with Al^{3+} (0–30 μM) in $\text{CH}_3\text{CN-H}_2\text{O}$ (9 : 1, v/v, pH 7.20, 10 mM HEPES buffer), $\lambda_{\text{ex}} = 400 \text{ nm}$. Inset shows Benesi-Hildebrand fitting of the data.

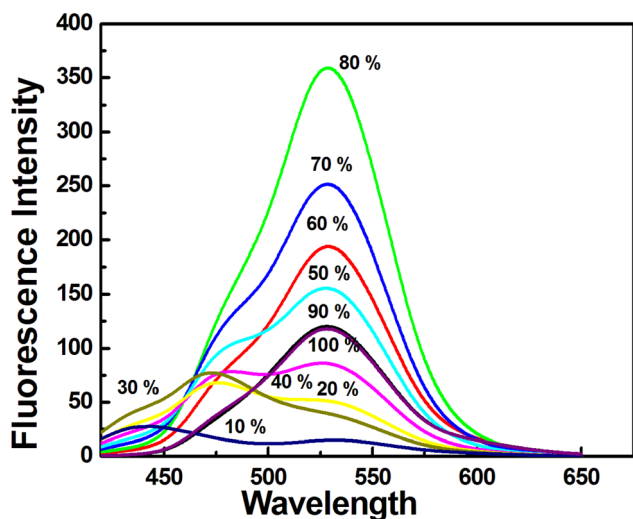


Fig. 3 Fluorescence emission of DFP-AMQ with different percent-ages of H₂O, $\lambda_{\text{ex}} = 400$ nm.

free DFP-AMQ and Al³⁺ leads to the chelation-enhanced fluorescence (CHEF) effect causing ~27-fold enhancement due to the increased structural rigidity of the formed complexes (Fig. 2). Upon excitation at 400 nm, the isosbestic point in the absorption spectra, in the beginning, there is a gradual increase in the fluorescence intensity (FI) at $\lambda_{\text{em}} = 561$ nm, then a blue shift occurs to $\lambda_{\text{em}} = 535$ nm with the increase in [Al³⁺] (Fig. 2). This shifting occurs due to the intramolecular charge transfer (ICT).³⁶

To analyse the binding constant from the fluorescence titration data, a linear form of the Benesi-Hildebrand equation (eqn (1)) was used, which gives the apparent dissociation constant $K_d = (20.2 \pm 0.03) \times 10^{-5}$ M. The binding constants value obtained from UV-Vis and the fluorescence titration data clearly indicate the agreement between two K_d values.

3.4 Selectivity study

The selectivity study showed that the probe could selectively detect Al³⁺ ions, which were not disturbed by other metal ions

such as biologically rich K⁺, Na⁺, Mg²⁺, and Ca²⁺ metal ions, various transition metal ions, namely Fe²⁺, Fe³⁺, Mn²⁺, Ni²⁺, Cr³⁺, Co²⁺, and Cu²⁺, and heavy metal ions such as Hg²⁺, Cd²⁺, Zn²⁺, and Pb²⁺, and there was no interference (Fig. S8†). The fluorescent chemosensor was found to bind Al³⁺ reversibly when it reacted with excess EDTA (Fig. S9†). Moreover, no major change in the emission spectra was found even on excess addition of the above-mentioned interfering metal ions (Fig. S8†).

3.5 Calculation of LOD

To determine the detection limit, fluorescence titration of DFP-AMQ with Al³⁺ was carried out by adding a micromolar concentration of Al³⁺ in DFP-AMQ (20 μ M) and by the 3 σ method. The LOD was calculated as follows:

$$\text{LOD} = 3 \times S_d/S$$

where, S_d is the standard deviation of the intercept of the blank (DFP-AMQ only) obtained from a plot of fluorescence intensity (FI) vs. [DFP-AMQ], and S is the slope obtained from the linear part of the plot of FI vs. [Al³⁺]. Using the 3 σ method calculation, the detection limit (LOD) of Al³⁺ was 1.11 μ M (Fig. S10†).

3.6 pH study

For real applications, the appropriate pH conditions required for the successful action of the sensor were estimated. The probe DFP-AMQ showed very weak fluorescence emission between pH 2 and 8, while the DFP-AMQ-Al complex showed very strong fluorescence emission between pH 5 and 8 in 10 mM HEPES buffer, clearly indicating that this pH range is suitable for fluorescence studies for the complexation with Al³⁺ (Fig. S11†). The fluorescence emission of free DFP-AMQ increases beyond pH 10.0 due to the acid dissociation of the proton.

3.7 Aggregation induced emission (AIE) of DFP-AMQ

AIE was observed when the percentage of water was varied. Here, CH₃CN and H₂O were used as good and poor solvents,

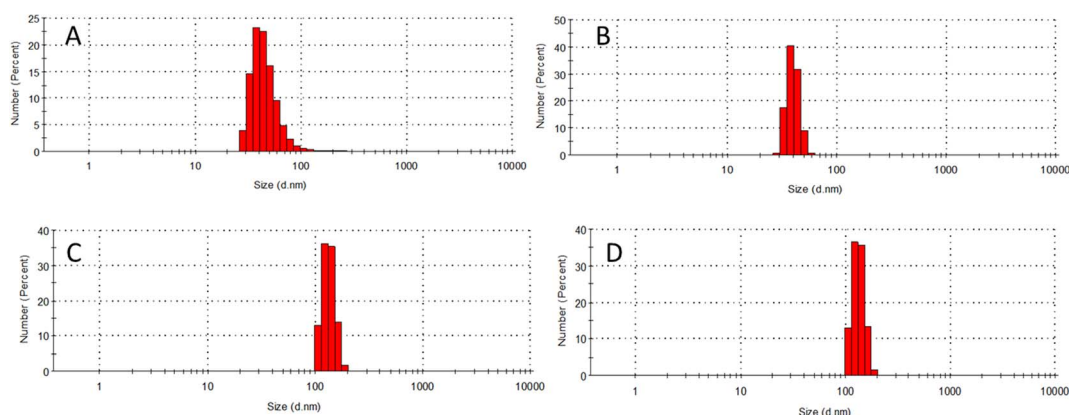


Fig. 4 Dynamic light scattering (DLS) study of DFP-AMQ with different percentages of H₂O: (A) 0%, (B) 20%, (C) 50%, and (D) 80% and shows the sizes (A) 40.48 nm, (B) 44.77 nm, (C) 142.8 nm and (D) 154.62 nm.

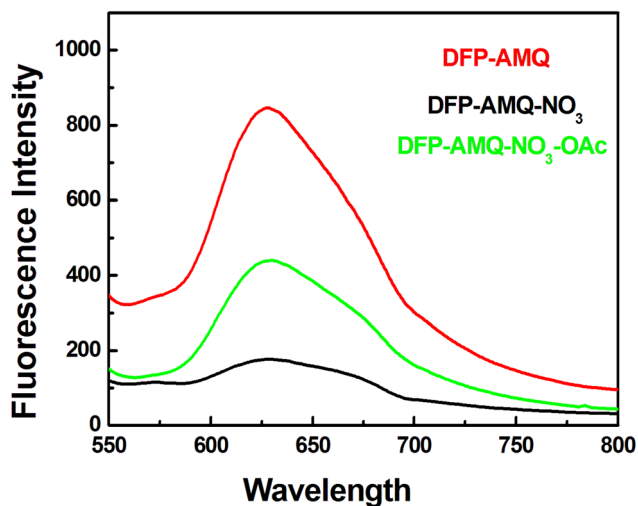


Fig. 5 Fluorescence emission of DFP-AMQ with NO_3^- and both NO_3^- - OAc^- in the solid state (at $\lambda_{\text{ex}} = 450 \text{ nm}$).

respectively. This study revealed that with increasing water percentages (0–100) the fluorescence emission increases towards the red region and at 80% of water content, it showed a maximum emission at 528 nm (Fig. 3). This observation clearly indicates the J-type aggregation induced emission due to the presence of a large π -conjugated planar structure. In the aggregates, however, DFP-AMQ molecules face strong face-to-

face π - π interactions between two DFP-AMQ molecules, and these are expressed directly by the overlaps in π -conjugated systems. In CH_3CN medium DFP-AMQ showed a typical AIE phenomenon having very weak fluorescence.

Upon increasing the volume of water percentages up to 80%, fluorescence emission enhancement occurred due to the emissive TICT state (quasi-TICT*). Upon further increase of water from 80 to 99 in vol%, the fluorescence emission intensity decreased, which is known. Due to the restriction of intramolecular motion (RIM) in the aggregated state ACQ effect occurs. Consequently, the formation of a planar structure from the twisted structure in the excited state is accountable for the solution state quenching.

3.8 DLS measurements

To realise the aggregation behaviour of DFP-AMQ, dynamic light scattering (DLS) experiments were performed in the presence of varying water percentages (Fig. 4). DLS studies revealed that the average size of the aggregated DFP-AMQ in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ ($f_w = 10\%$) was *ca.* 40.48 nm, as shown in Fig. 4A. This also signifies that DFP-AMQ can be well-dissolved and dispersed in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ solution. However, an increase in the volume of the water percentage (up to 80%) led to a significant increase in the average size of aggregates (Fig. 4D), which also supported the observed AIE activity of the probe DFP-AMQ. While, the average size of the aggregates became 154.62 nm in 80% volume

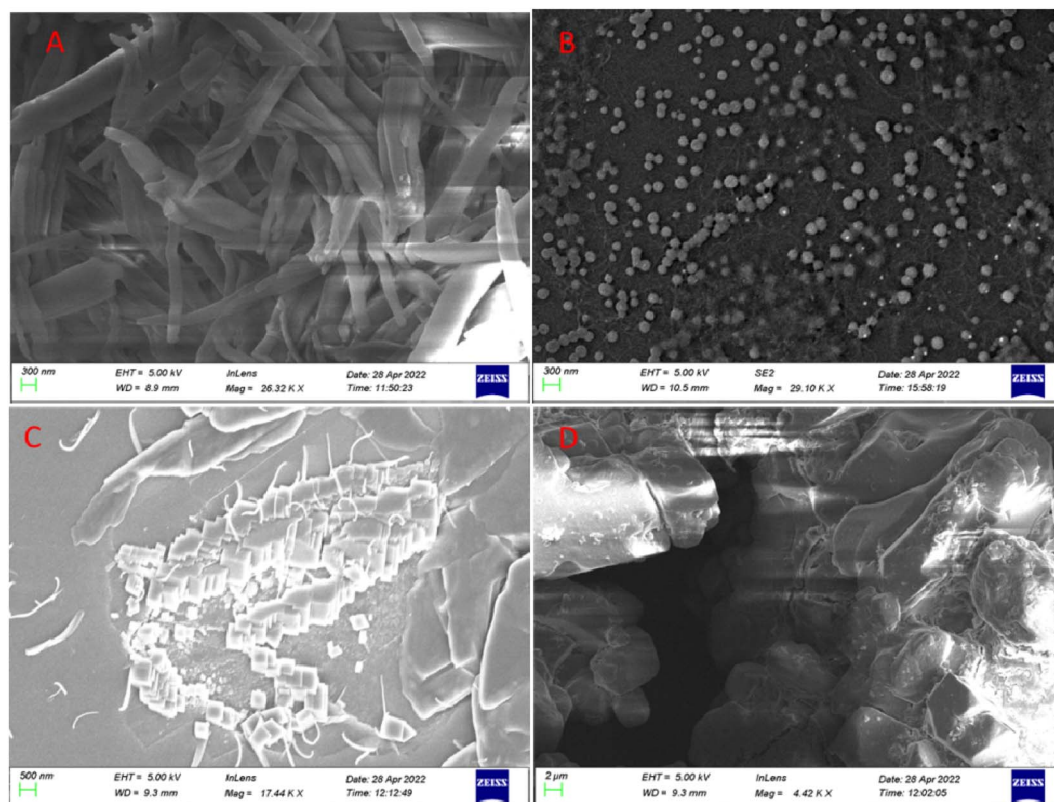


Fig. 6 SEM images of (A) DFP-AMQ (solid sample), (B) $[\text{DFP-AMQ-Al}]^+$ (solid sample), (C) DFP-AMQ in the presence of H_2O , (D) DFP-AMQ-nitrate-acetate.

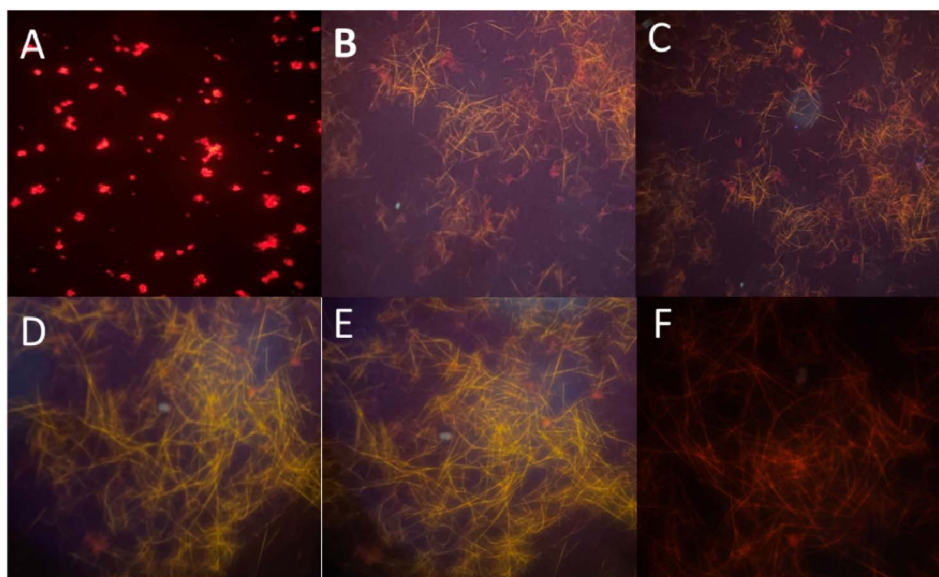


Fig. 7 Fluorescence microscope images of (A) DFP-AMQ, DFP-AMQ in the presence of (B) 20% H₂O, (C) 50% H₂O, (D) 70% H₂O, (E) 80% H₂O and (F) 100% H₂O.

percentage of water (Fig. 4D), which is in good agreement with the spectroscopic studies.

Now to prove the aggregation behavior of DFP-AMQ in the presence of Al³⁺ ions, we also carried out the DLS measurements in the presence of 0%, 20%, and 50% water. However, an increase in the volume of water percentage led to a significant increase in the average size of aggregates (Fig. S12[†]), which also supported the observed AIE activity of the probe DFP-AMQ in the presence of Al³⁺. The average sizes of the above solutions are 204.04 nm, 297.41 nm, and 315.27 nm, respectively.

3.9 Solid state emission

The solid-state emission spectra of DFP-AMQ were measured at $\lambda_{\text{ex}} = 450$ nm and its fluorescence intensity (FI) was found at $\lambda_{\text{em}} = 628$ nm. DFP-AMQ showed fluorescence emission due to the aggregation, which is clearly indicated by the scanning electron microscope studies. When the solid DFP-AMQ was ground in a mortar pastel with solid sodium nitrate, the emission decreased and after that, this material was ground with solid sodium acetate, and again the emission spectra were observed with very high intensity, almost double that of the solid DFP-AMQ-NO₃. We also recorded the emission spectra with other anion salts, but only the acetate ion responded (Fig. S13[†]). Hence, this study revealed that in the solid state after grinding with sodium nitrate, it recognized only acetate ions (Fig. 5).

3.10 SEM study

The morphologies of DFP-AMQ, its Al-complex, DFP-AMQ in 80% water, and DFP-AMQ with nitrate and DFP-AMQ-nitrate-acetate were studied using the scanning electron microscopy (SEM) analysis, which provided the evidence for the changes in the morphology of DFP-AMQ (rod-like shape) to DFP-AMQ-Al

(spherical-like shape) aggregate formation of DFP-AMQ-H₂O (aggregated-block-like shape), DFP-AMQ with nitrate (no particular shape) and DFP-AMQ-nitrate-acetate (stone-like shape) (Fig. 6).

3.11 Fluorescence microscope imaging

Fluorescence microscope images show that the solid DFP-AMQ showed fluorescent images after treatment with different percentages of water in the solution state and after drop casting on the slide, needle-like aggregated shapes were found (Fig. 7).

3.12 Time-correlated single photon counting measurements

Time-correlated single-photon counting measurements for the lifetime experiments for the DFP-AMQ in CH₃CN and CH₃CN-H₂O and DFP-AMQ-Al³⁺ were performed. For the pure CH₃CN, the lifetime of DFP-AMQ was 0.09 ns but in the organic aqueous medium, the lifetime increased to 4.59 ns due to its aggregation behavior, while the complex showed a lifetime of 9.58 ns (Fig. S14[†]).

4. Conclusion

In summary, we have successfully designed and synthesized a DFP-AMQ-based hexa-coordinating N₂O donor ligand that selectively recognizes Al³⁺ colorimetrically and fluorimetrically with ~27-fold fluorescence enhancement in the presence of a number of various interfering metal ions, and it was found to undergo 1:1 complexation in MeCN-H₂O (9:1, v/v, pH 7.2, HEPES buffer). By blocking ESIPT, chelation-enhanced fluorescence effect (CHEF) arose and the resulting fluorescence enhancement was observed. The complexation of DFP-AMQ to Al³⁺ was confirmed by ¹H NMR and HRMS studies. The *K*_d values measured were $3.26 \times 10^{-5} \text{ M}^{-1}$ and $2.02 \times 10^{-5} \text{ M}^{-1}$

obtained from the UV-Vis and fluorescence titrations, respectively, revealing the strong binding towards Al^{3+} ions. The limit of detection of Al^{3+} by **DFP-AMQ** was $1.11 \mu\text{M}$. The quantum yields of the **DFP-AMQ** and $[\text{DFP-AMQ-Al}]^+$ were 0.008 and 0.211, respectively. Dynamic light scattering (DLS) studies showed an increase in the sizes of the particles with increasing water percentage and this was due to aggregation. Under the different reaction conditions, SEM studies revealed interesting microstructures. The rod-like shape of **DFP-AMQ** was converted to a spherical-like shape in the presence of Al^{3+} ions, whereas the block-like shape of the aggregated **DFP-AMQ** occurring in H_2O was observed. In the solid phase, **DFP-AMQ** with nitrate had no particular shape, but in the presence of acetate, it was converted to a stone-like shape. The observed results indicate that this probe (**DFP-AMQ**) is very much useful for on-site Al^{3+} ions detection in the solid state through a fast, simple, and eco-friendly process; it may be useful in OLED and to develop biomedicine for Alzheimer's and Parkinson's diseases.

Conflicts of interest

The authors declare no conflicts of interest.

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