

Supporting Information

Aluminium fluorosensor for early detection of micro-level alcoholate corrosion

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General experimental procedure

Unless otherwise stated, chemicals and solvents of analytical grade were purchased from Sigma-Aldrich (USA) and were used without further purification. However, solvents for spectroscopic studies were dried meticulously by usual procedure. ^1H NMR and ^{13}C NMR studies of HMBDC and HMBDC/ Al^{3+} complex were carried out in $\text{DMSO-}d_6$ and CD_3OD medium, respectively, with Bruker 300-MHz NMR spectrometer. ESI- MS^+ in the positive mode were carried out with a QTOF Micro YA263 mass spectrometer. Thermo gravimetric analysis (TGA) was performed in Pyris6 TGA (Netherlands) instrument. Cyclic Voltammetry (CV) was carried out in AutoLab (PG State 001) instrument with a platinum electrode (4-mm diameter) as the working electrode and the results were collected with reference to the standard calomel electrode. IR spectra in methanol medium were recorded by a Perkin-Elmer Spectrum-2 spectrophotometer equipped with a Zn-Se ATR. Surface morphology of aluminium alloy, Al-7075, before and after corrosion were performed using Field Emission Scanning Electron Microscope (JSM 6700F, JEOL Ltd. Tokyo, Japan).

Synthesis of Schiff base (HMBDC)

2-hydroxy-3-(hydroxymethyl)-5-methylbenzaldehyde (HHMB) was prepared according to the published procedure starting from p-cresol.¹ For synthesis of HMBDC ((6Z)-6-(2-hydroxy-3-(hydroxymethyl)-5-methylbenzylideneamine)-2H-chromen-2-one) to an anhydrous ethanolic solution of HHMB (0.04 g, 0.25 mmol), 6-amino-2H-chromen-2-one (6-ACO) (0.04 g, 0.20 mmol) was added drop wise at ambient condition with constant stirring and further 2 drops of AcOH were added to it. Then the mixture was refluxed for 2 hr at 40°C followed by filtration. The filtrate was then evaporated under reduced pressure to get the crude product as gel. It was purified by column chromatography followed by rotary evaporation to obtain the pure HMBDC and dried over CaCl_2 under vacuum. The structural analyses were performed by ^1H , ^{13}C -NMR and ESI- MS^+ . ^1H NMR ($\text{DMSO-}d_6$, 300-MHz): 2.18-2.28 (s, 3H, ArCH_3), 2.48-3.31 (due to trace H_2O in the solvent $\text{DMSO-}d_6$), 4.54-4.56 (d, 2H, $\text{CH}_2\text{-OH}$), 5.09 (t, 1H, $\text{-CH}_2\text{-OH}$), 6.53-6.57 (d, 1H, CH=CH), 7.29 (s, 1H, ArH), 7.36 (s, 1H, ArH), 7.47-7.50 (d, 1H, ArH), 7.69-7.71 (d, 1H, CH=CH), 7.78 (s, 1H, ArH) 8.05-8.08 (d, 1H, -ArH), 8.96 (s, 1H, -N=CH), 13.14 (s, 1H, ArOH), ppm. ^{13}C NMR ($\text{DMSO-}d_6$, 75 MHz): 20.66, 57.82, 117.41, 117.91, 118.33, 119.83, 121.16, 125.53, 127.67, 130.23, 131.39, 132.49, 144.46, 144.63, 152.66, 155.66, 160.29, 165.04 ppm (Fig. S1). ESI- MS^+ for HMBDC in methanol: m/z Cal for $[\text{HMBDC}+\text{H}]^+$: 310.3207; Found: 310.3972 (Fig. S5A).

UV-vis absorption and fluorescence studies

UV-vis absorption studies using 1-cm path length quartz cell were carried out with a double beam spectrophotometer (Shimadzu, Japan; model TCC-240A) equipped with a thermostated cell holder. Steady state fluorescence measurements were done in Perkin Elmer LS-55 spectrofluorimeter (Perkin Elmer, USA) using 1-cm path length quartz cell. Fluorescence spectra were obtained for excitation at 406 nm (excitation band-pass: 8, emission band pass: 3). The measuring solutions were filtered using a 0.45 mm filter (Millex, Millipore). The spectral reproducibility was verified by triplicate measurements.

Limit of detection studies

The Al³⁺ detection limit was evaluated from the equation below:²

$$\text{Detection limit} = K \times S_{\text{bi}} \times S \quad (2)$$

Here, $K = 3$, as per IUPAC convention. S_{bi} = experimental standard deviation for the blank, and S = slope of the fluorescence increase with respect to Al³⁺ concentration. The Al³⁺ detection limit was estimated to ~0.5 μM in anhydrous methanol medium.

Theoretical calculations

Gaussian 09 Program was used to perform DFT and time-dependent DFT (TD-DFT) calculations stated in this work.³ Geometry depends on most acceptable structure was bring off by considering B3LYP exchange-correlation functional for ligand (HMBDC) and its complex with Al³⁺. The 6-31G+(d,p) basis was set for H, C, N, O atoms and the geometries were optimized in solvent phase. The global minima of all these species were confirmed by the positive vibrational frequencies. TD-DFT calculation in methanol medium was performed for investigating the electronic properties of the singlet excited state using optimized geometries of the ground (S_0) states of the relevant species, along with determination of vertical excitation energy and oscillator strength of the respective ground state geometry.

Fluorometric corrosion studies

Pure aluminium sheet and its alloy sheet, namely, Al-7075 (composition: Al, 90%; Zn, 5.5%; Mg, 2.5%; Cu, 1.5 and Si, 0.5%) with same dimension (3.5 cm \times 1.5 cm \times 0.2 cm) were grazed with a grade emery papers (400 grade) for surface finish purpose. The finished metal sheets washed thoroughly in acetone and then sonicated for 30 min. Finally, the specimens were washed with deionized water, and then dried at 60°C for 20 min in an oven. The weight of those metallic sheets were determined using METTLER AE 240 balance. These coupons were

then fully immersed in a 10 or 100 mL anhydrous methanol or 4:1 (v/v) methanol/ethanol mixed medium within air-tight measuring flux under the normal air and nitrogen conditions. To maintain appropriate normal air or nitrogen condition throughout the course of corrosion (up to 30 days), the open air or nitrogen was purged in every 24 hr interval, where the small change in solution volume was adjusted if required by injecting appropriate amount of normal air- or nitrogen-saturated same solvent. To detect amount of Al(OR)₃ formation due to the alcoholate corrosion, 30 µL corrosion solution in every three-days' time-intervals up to 18 or 30 days was taken out using a syringe, and the fluorescence measurement was performed after diluting the corrosion solution with 270 µL of parent solvent. To measure the weight-loss due to corrosion, the metallic sheet was taken out from the medium after certain time-interval (after 18 days for pure aluminium sheet) and dried properly in oven. The weight of the metallic sheet after the corrosion was estimated using the balance mentioned before.

Electrochemical studies

Electrochemical properties of the corrosion medium for the aluminium alloy in absence and presence of externally added water were investigated using cyclic voltammetric technique for methanol/ethanol (4:1 v/v) medium with a computer controlled Potentiostat/Galvanostat instrument (AUTOLAB, Netherland) along with a conventional three electrode system at room temperature. Tetrabutyl ammonium perchlorate was used as supporting electrolyte. The Pt-wire was used as the working electrode and saturated calomel electrode (SCE) as reference electrode and Pt-foil electrode (1 cm × 1 cm) as the counter electrode. Cell operation condition: scan region, -1.2V to 0.4 V and scan rate, 0.05 V/s.

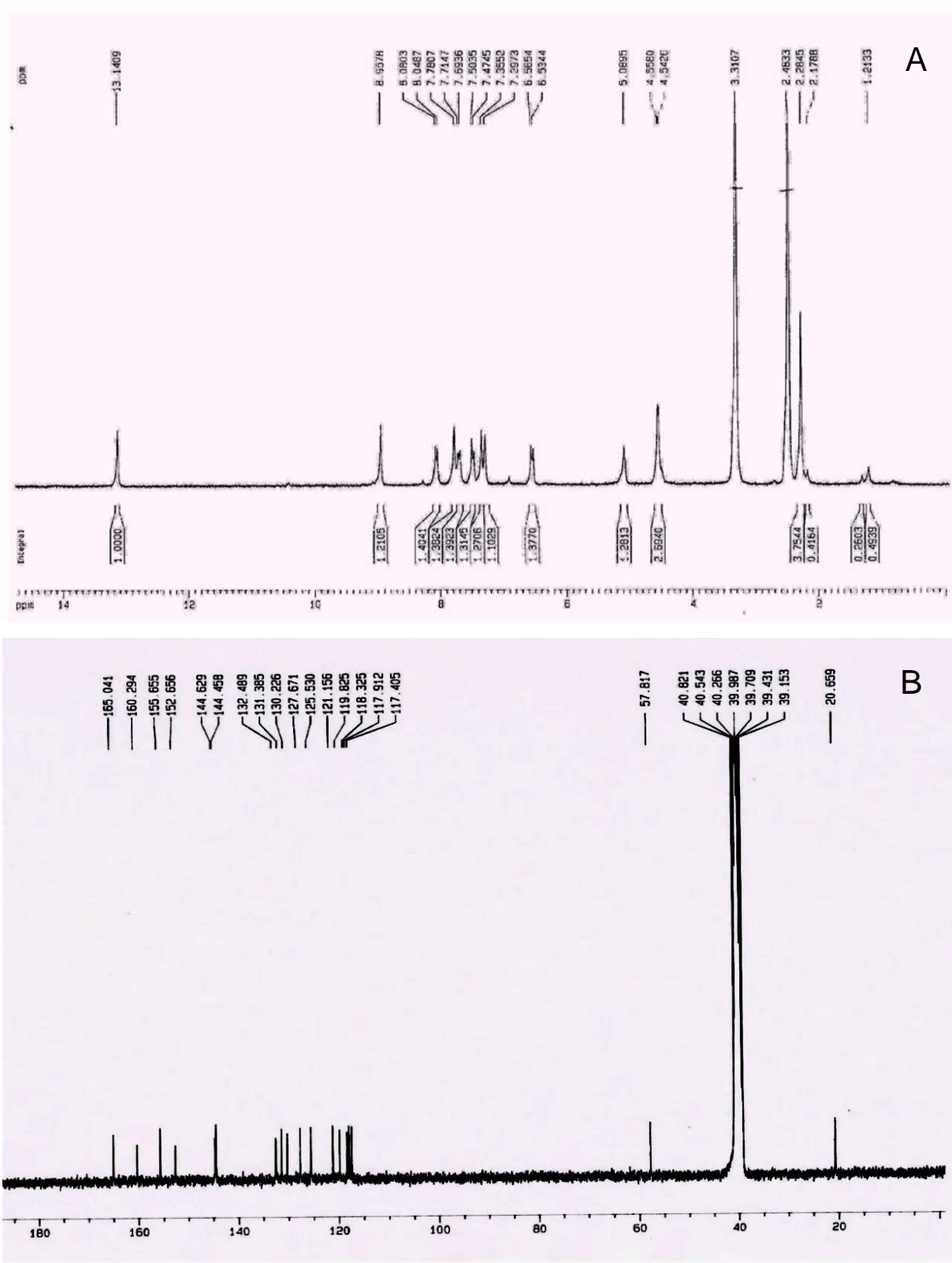


Fig. S1. (A) $^1\text{H-NMR}$ and (B) $^{13}\text{C-NMR}$ spectra of HMBDC in $\text{DMSO-}d_6$.

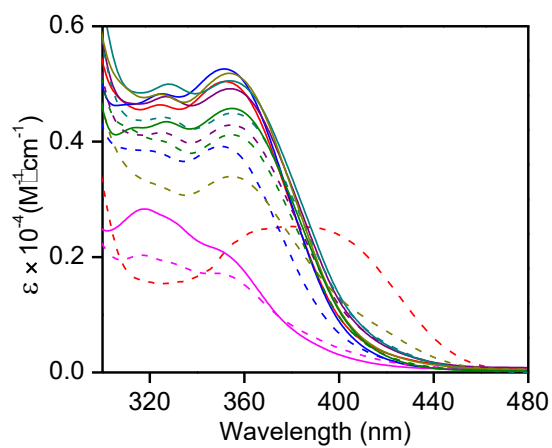


Fig. S2. Solvent dependent UV-vis absorption spectra of HMBDC in the absence (solid lines) and presence (broken lines) of $\text{Al}(\text{NO}_3)_3$ (8 equiv.) at 25°C : methanol (red), acetonitrile (blue), 1,4-dioxane (magenta), DMF (purple), DMSO (pink), ethanol (dark yellow) and THF (green).

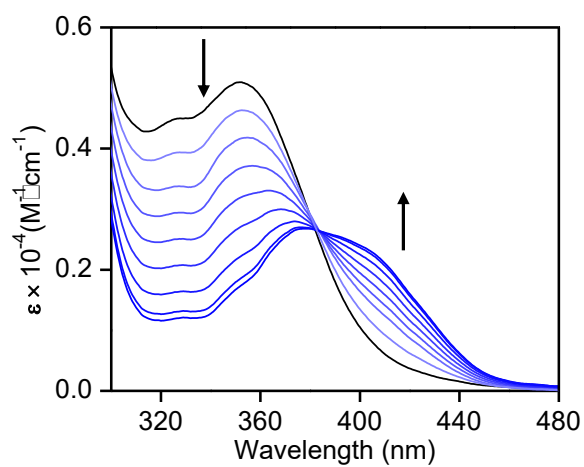


Fig. S3. UV-vis absorption spectra of HMBDC (5 μM) in presence of increasing concentration of $\text{Al}(\text{NO}_3)_3$ (up to 25 μM) in 4:1 (v/v) methanol/ethanol mixed medium at 25°C. The increase or decrease of absorbance with increasing concentration of Al^{3+} is depicted by the arrows. The spectrum in the absence of Al^{3+} is shown by black.

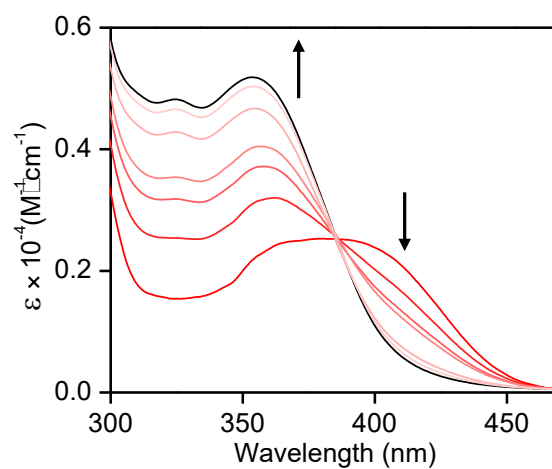


Fig. S4. UV-vis absorption spectral changes for HMBDC/Al³⁺ (5 μM with respect to HMBDC) in methanol by addition of increasing amount of water (0–20% (v/v)). The increase or decrease of absorbance with increasing amount of water is depicted by the arrows. The spectrum of HMBDC in methanol is shown by black.

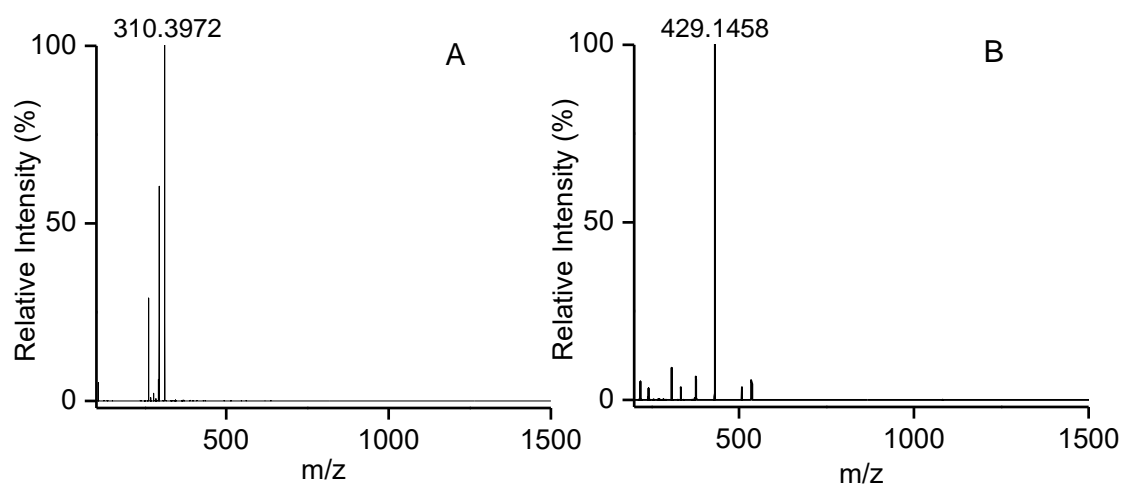


Fig. S5. ESI-MS⁺ of HMBDC (A) (m/z for [HMBDC+H]⁺ or [C₁₈H₁₆O₄N]⁺: cal'd – 310.3207 (obs'd – 310.3972)) and HMBDC/Al³⁺ complex (B) (m/z for [HMBDC+Al+NO₃+CH₃OH]⁺ or [C₁₉H₁₉O₈N₂Al]⁺: cal'd – 429.3315 (obs'd – 429.1458) in MeOH.

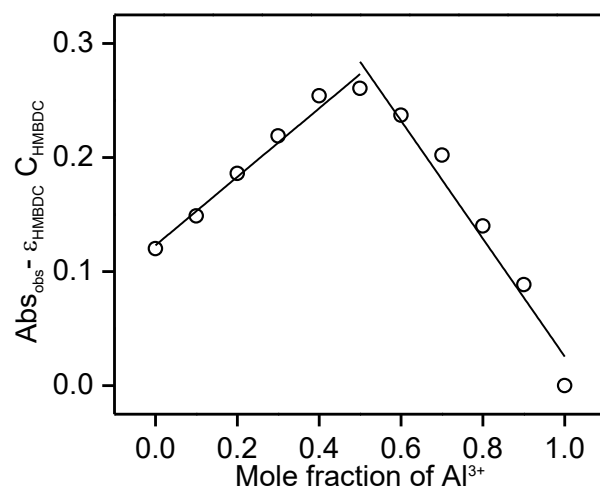


Fig. S6. Job's plot for defining binding stoichiometry of Al³⁺ to HMBDC in methanol medium, at 25°C.

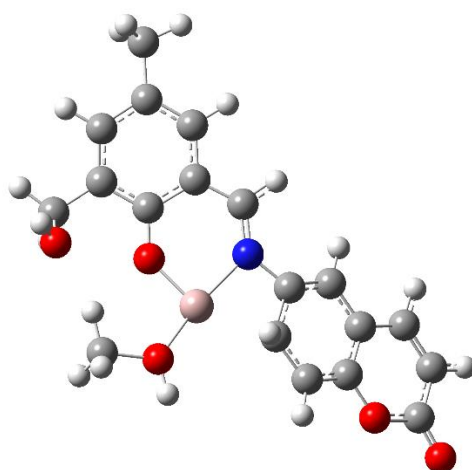


Fig. S7. Molecular view of HMBDC/Al³⁺ complex optimized with DFT-based theoretical calculation: (color code) white, H; gray, C; blue, N; red, O and light pink, Al.

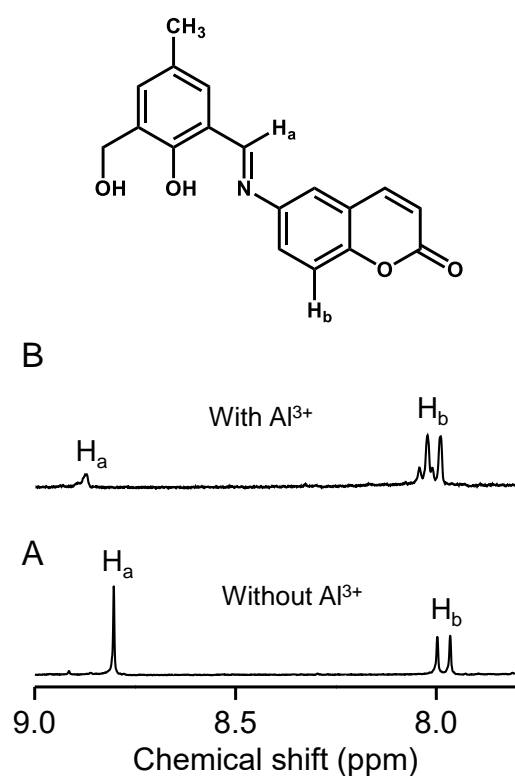


Fig. S8. 300 MHz ¹H-NMR (downfield region) spectra of HMBDC in (A) the absence and (B) presence of 8.0 equiv. of Al(NO₃)₃ in CD₃OD.

Note: The full-scale spectra were not shown for clarity. With change in solvent DMSO-*d*₆ (Fig S1) to CD₃OD phenolic-OH and benzylic-OH protons peaks were abolished due to H/D exchange.

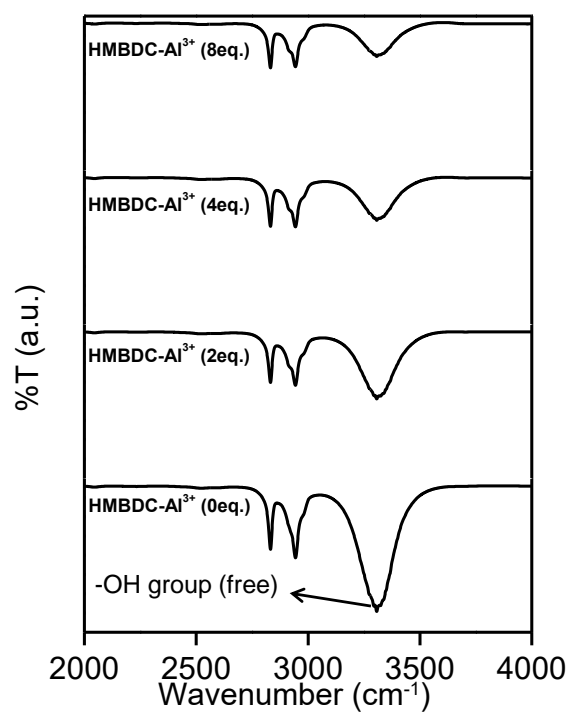


Fig. S9. FT-IR spectra of HMBDC in the absence and presence of various concentration of Al(NO₃)₃ in methanol medium.

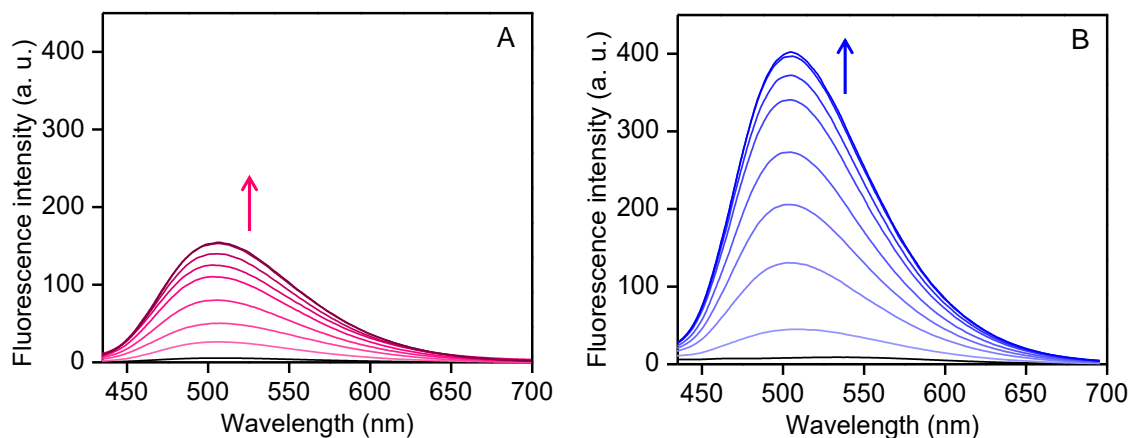


Fig. S10. Fluorescence spectra of HMBDC (5 μM) in presence of increasing concentration of Al(NO₃)₃ in (A) ethanol (up to 8 equiv.) and (B) methanol/ethanol (4:1 v/v) (up to 5 equiv.) at 25°C. The spectra without Al³⁺ are represented by black. The gradual increase of intensity with increasing concentration of Al³⁺ is shown by the arrow. The excitation wavelength was 406 nm.

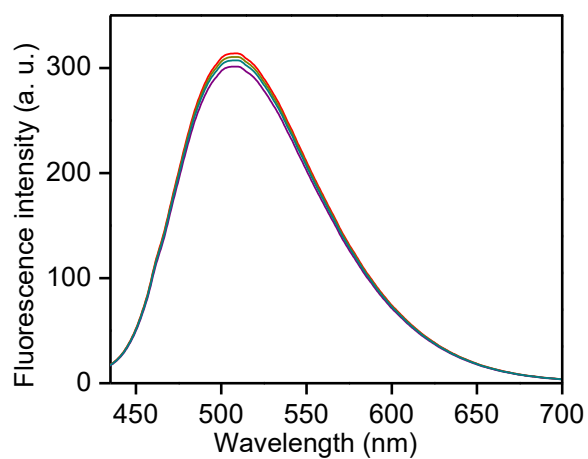


Fig. S11. Fluorescence spectra of HMBDC (5 μM) in the presence of various Al³⁺ salts (40 μM each): AlCl₃ (dark yellow), Al(NO₃)₃ (red), Al₂(SO₄)₃ (purple), and Al(OEt)₃, green.

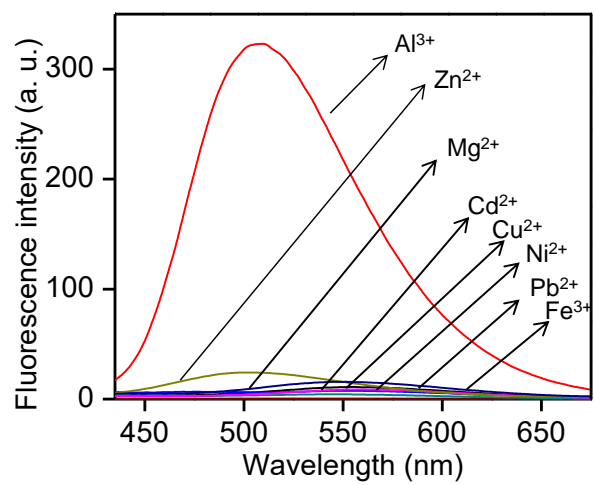


Fig. S12. Fluorescence spectra of HMBDC (5 μM) in methanol medium containing different metal ions (40 μM each).

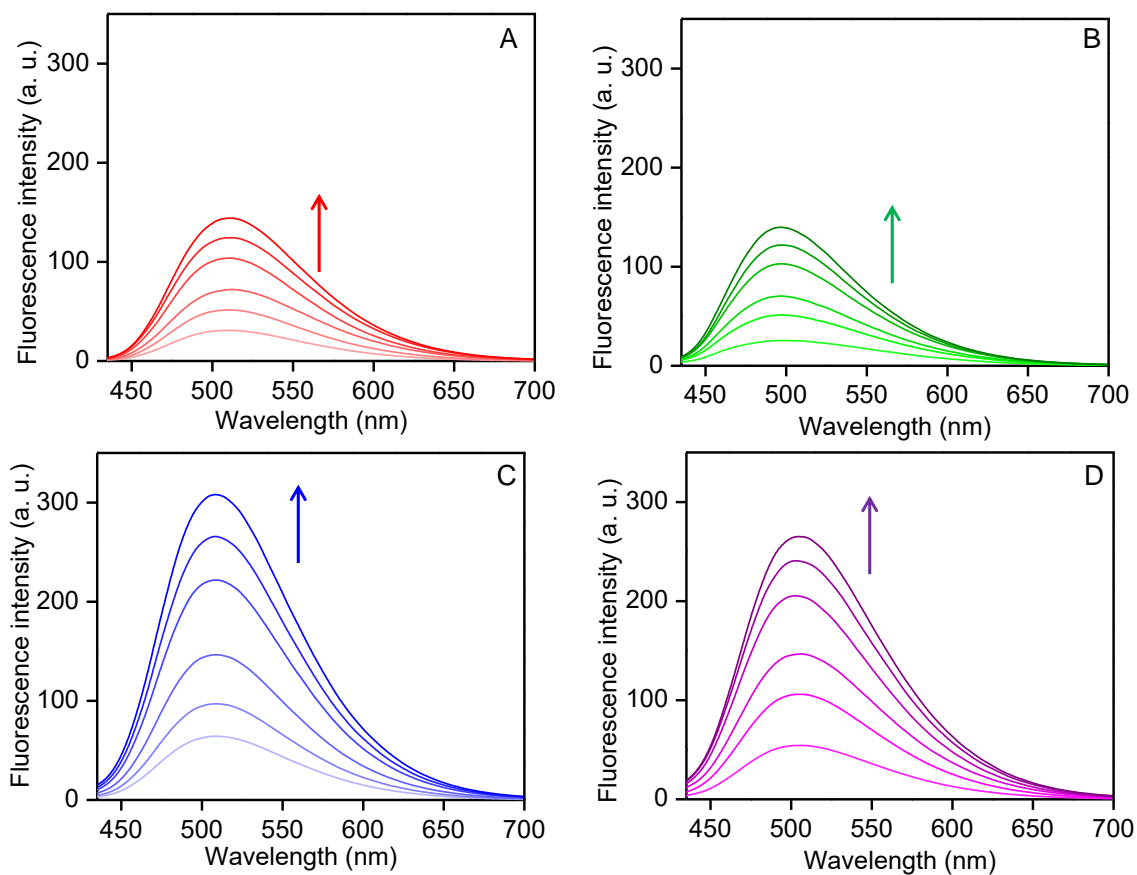


Fig. S13. Fluorescence spectra of HMBDC for the corrosion of pure aluminium sheet (dimension: $3.5 \times 1.5 \times 0.2 \text{ cm}^3$). The spectra of HMBDC ($5 \mu\text{M}$) in alcohol medium (methanol or 4:1 (v/v) methanol/ethanol mixture) containing 10% corrosion solution of same solvent composition after undergoing the corrosion at every 3-days' time-interval up to 18 days at nitrogen or open air condition: (A) methanol in nitrogen condition; (B) methanol in open air condition; (C) 4:1 (v/v) methanol/ethanol medium at nitrogen condition, (D) 4:1 (v/v) methanol/ethanol medium at open air condition. The increase of intensity with increasing incubation time (3 to 18 days) are depicted by arrows.

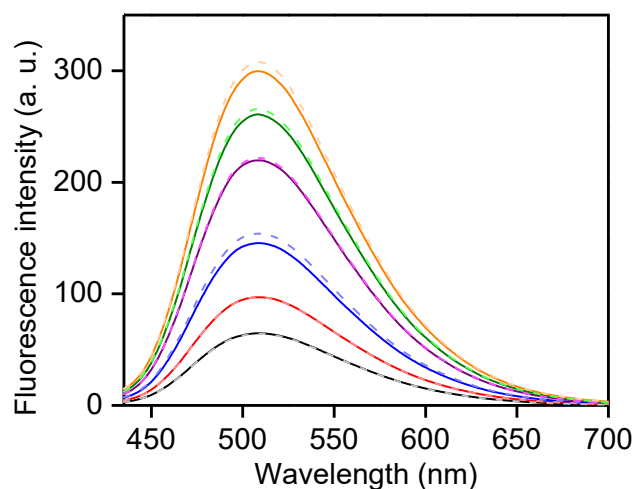


Fig. S14. Changes in fluorescence spectra of HMBDC due to various amount of $\text{Al}(\text{OEt})_3$ addition at different time-intervals in 100 mL 4:1 (v/v) methanol/ethanol medium at open air condition. After addition of $\text{Al}(\text{OEt})_3$ at day-0 (beginning of day 1), 3.2 μmol ; day-3, 5.7 μmol ; day-6, 8.0 μmol ; day-9, 11.7 μmol ; day-12, 14.2 μmol ; day-15, 16.4 μmol , the fluorescence were monitored after (black) day-3, (red) 6, (blue) 9, (purple) 12, (green) 15, and (orange) 18, respectively. The fluorescence intensity of HMBDC (5 μM) were monitored after 10-fold dilution of the medium containing $\text{Al}(\text{OEt})_3$ with the same solvent. The fluorescence were recorded before the addition of day-specific schedule $\text{Al}(\text{OEt})_3$ amount (solid lines). The amount of $\text{Al}(\text{OEt})_3$ represents sum of all additions. For comparison, the fluorescence spectra for the corrosion medium at the same time interval as shown in Fig S14C are depicted by the corresponding light color spectra (broken lines).

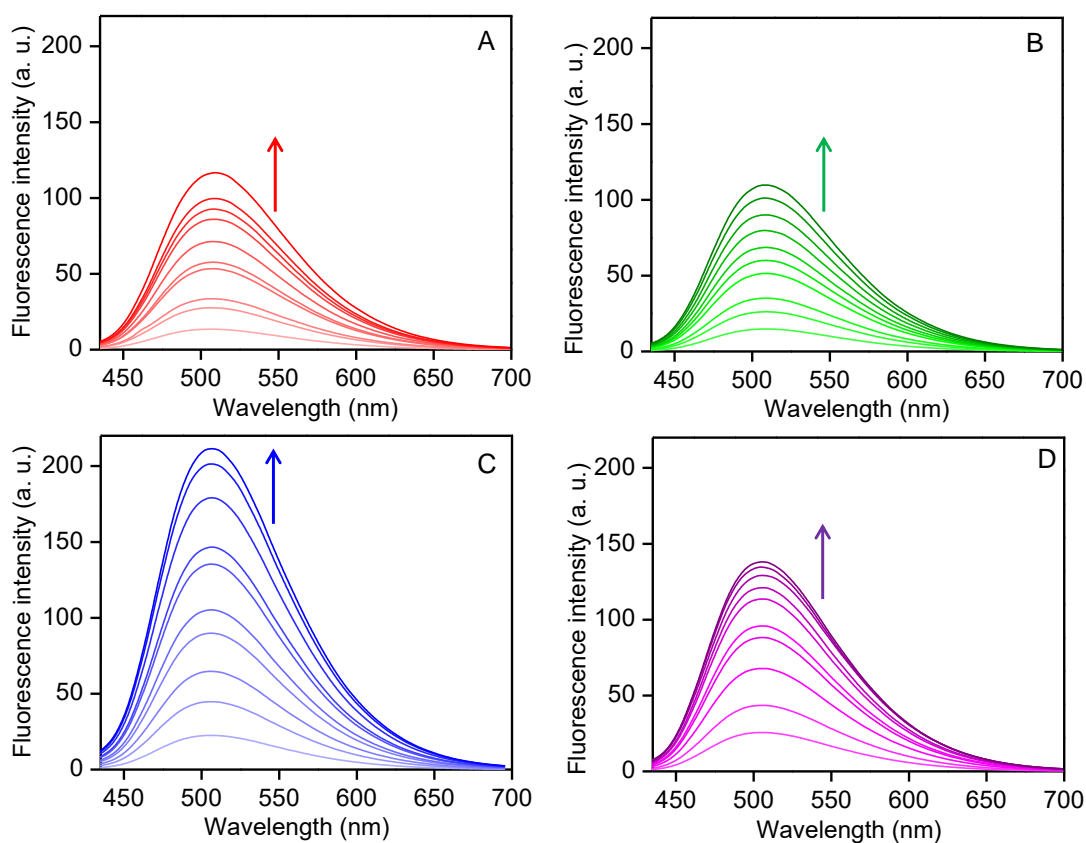


Fig. S15. Fluorescence spectra of HMBDC for the corrosion of aluminium alloy sheet, Al-7075 (dimension: $3.5 \times 1.5 \times 0.2 \text{ cm}^3$). The spectra of HMBDC ($5 \mu\text{M}$) in alcohol medium (methanol or 4:1 (v/v) methanol/ethanol mixture) containing 10% corrosion medium of same solvent composition after undergoing the corrosion at every 3-days' time-interval up to 30 days at nitrogen or open air condition: (A) methanol in nitrogen condition; (B) methanol in open air condition; (C) 4:1 (v/v) methanol/ethanol medium at nitrogen condition, (D) 4:1 (v/v) methanol/ethanol medium at open air condition. The increase of intensity with increasing incubation time (3 to 30 days) are depicted by arrows.

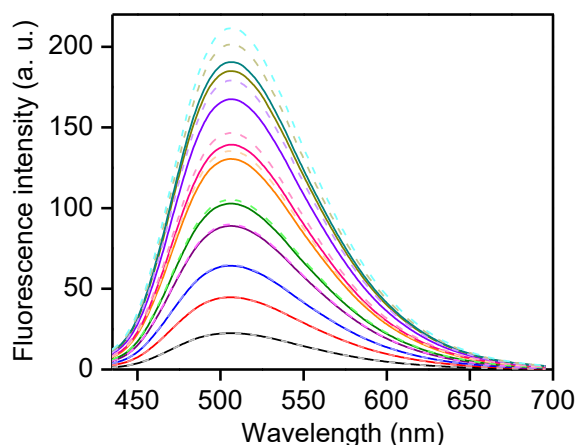


Fig. S16. Changes in fluorescence spectra of HMBDC due to various amount of $\text{Al}(\text{OEt})_3$ addition at different time intervals in 100 mL 4:1 (v/v) methanol/ethanol medium at open air condition. After addition of $\text{Al}(\text{OEt})_3$ in day-0 (beginning of day 1), 1.2 μmol ; day-3, 2.4 μmol ; day-6, 3.5 μmol ; day-9, 4.8 μmol ; day-12, 5.7 μmol ; day-15, 7.2 μmol ; day-18, 7.9 μmol ; day-21, 9.6 μmol ; day-24, 10.8 μmol and day-27, 11.4 μmol , the fluorescence were monitored after day 3 (black), 6 (red), (blue) 9, (purple) 12, (green) 15, (orange) 18, (pink) 21, (violet) 24, (dark yellow) 27, and (dark cyan) 30, respectively. The fluorescence intensity of HMBDC (5 μM) were monitored after 10-fold dilution of the medium containing $\text{Al}(\text{OEt})_3$ with the same solvent. The fluorescence were recorded before the addition of day-specific schedule $\text{Al}(\text{OEt})_3$ amount (solid lines). The amount of $\text{Al}(\text{OEt})_3$ represents sum of all additions. For comparison, the fluorescence spectra for the corrosion medium at the same time interval as shown in Fig S16C are depicted by corresponding light color spectra (broken lines).

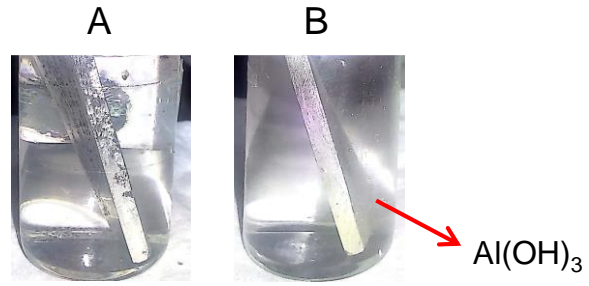


Fig. S17. Naked eye corrosion monitoring for Al-7075 sheet (dimension: $3.5 \times 1.5 \times 0.2 \text{ cm}^3$) after 30 days' time-period in 10 mL 4:1 (v/v) methanol/ethanol medium at (A) nitrogen and (B) open air conditions.

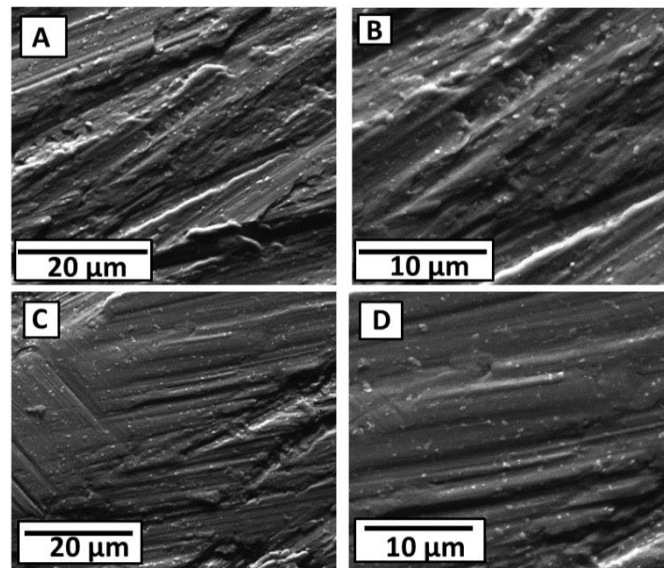


Fig. S18. FESEM images of Al-7075 alloy (A,B) before and after (C,D) corrosion in (A,C) methanol and (B,D) 4:1 (v/v) methanol/ethanol medium.

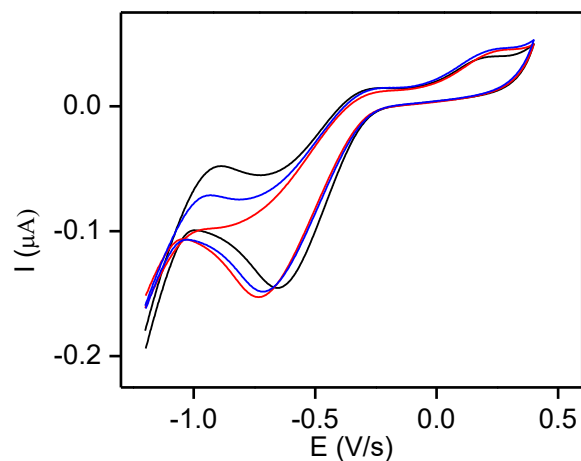


Fig. S19. Cyclic voltammetric studies in the corrosion medium for 4:1 (4:1) methanol/ethanol solution with Al-7075 alloy: (red) under nitrogen atmosphere and (blue) under open air condition. The cyclic votagram of the corrosion medium in the presence of externally added 2% water is depicted by black for comparison. Tetrabutyl ammonium perchlorate used as the supporting electrolyte. The potential were measured using platinised platinum electrode against saturated calomel electrode at 25°C. Scan region -1.2 to 0.4 V and scan rate 0.05 V/Sec.

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