Electronic Supporting Information

A Fluorescence 'turn-on' chemodosimeter for selective detection of Nb^{5+} ions in mixed aqueous media

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Instruments and experimental procedures

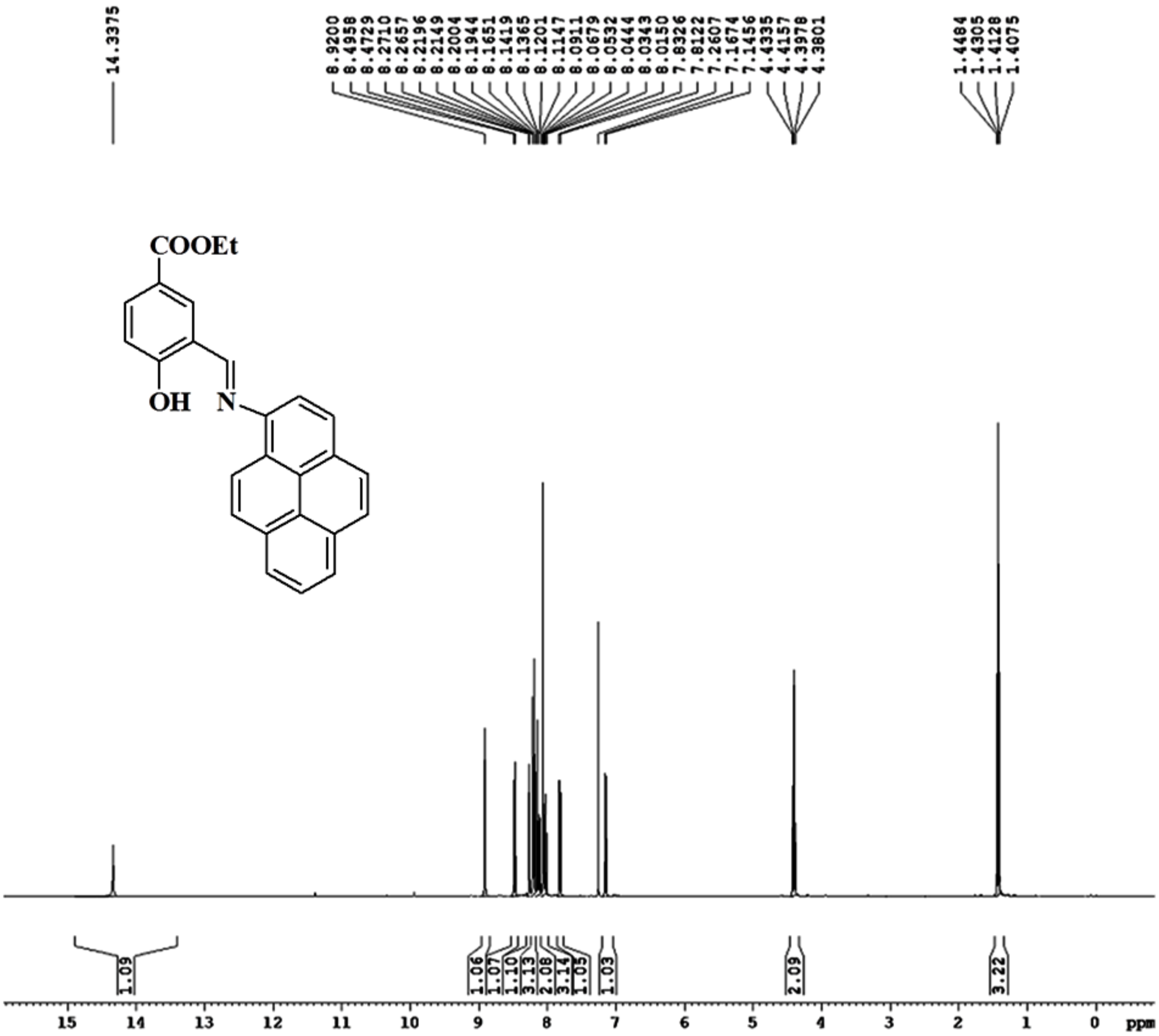
All reagents were purchased from Sigma Aldrich and were used without further purification. HPLC grade THF was used to perform analytical studies. All the fluorescence spectra were recorded on Agilent Technologies Cary Eclipse fluorescence spectrometer. UV-Vis spectra were recorded on Shimadzu UV-2450 spectrophotometer and FT-IR spectra were recorded on PerkinElmer FT-IR spectrometer (Spectrum Two, Serial No:88689). ESI-MS spectra were recorded by using Waters-Q-Tof Premier-HAB213 instrument. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance II 400 NMR spectrometer using $CDCl_3$ or DMSO-d_6 as solvents and TMS as internal standard. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, br = broad singlet, m = multiplet), coupling constant J (Hz), integration, and interpretation. Solution of compound **3** and metal chlorides were prepared in THF/H_2O (95:5, v/v). The H_2O used for making THF/H_2O mixtures was buffered with HEPES, pH = 7.0.[1]

1. D. D. Perrin, B. Dempsey, *Buffers for pH and Metal Ion Control*; John Wiley & Sons: New York, 1974.

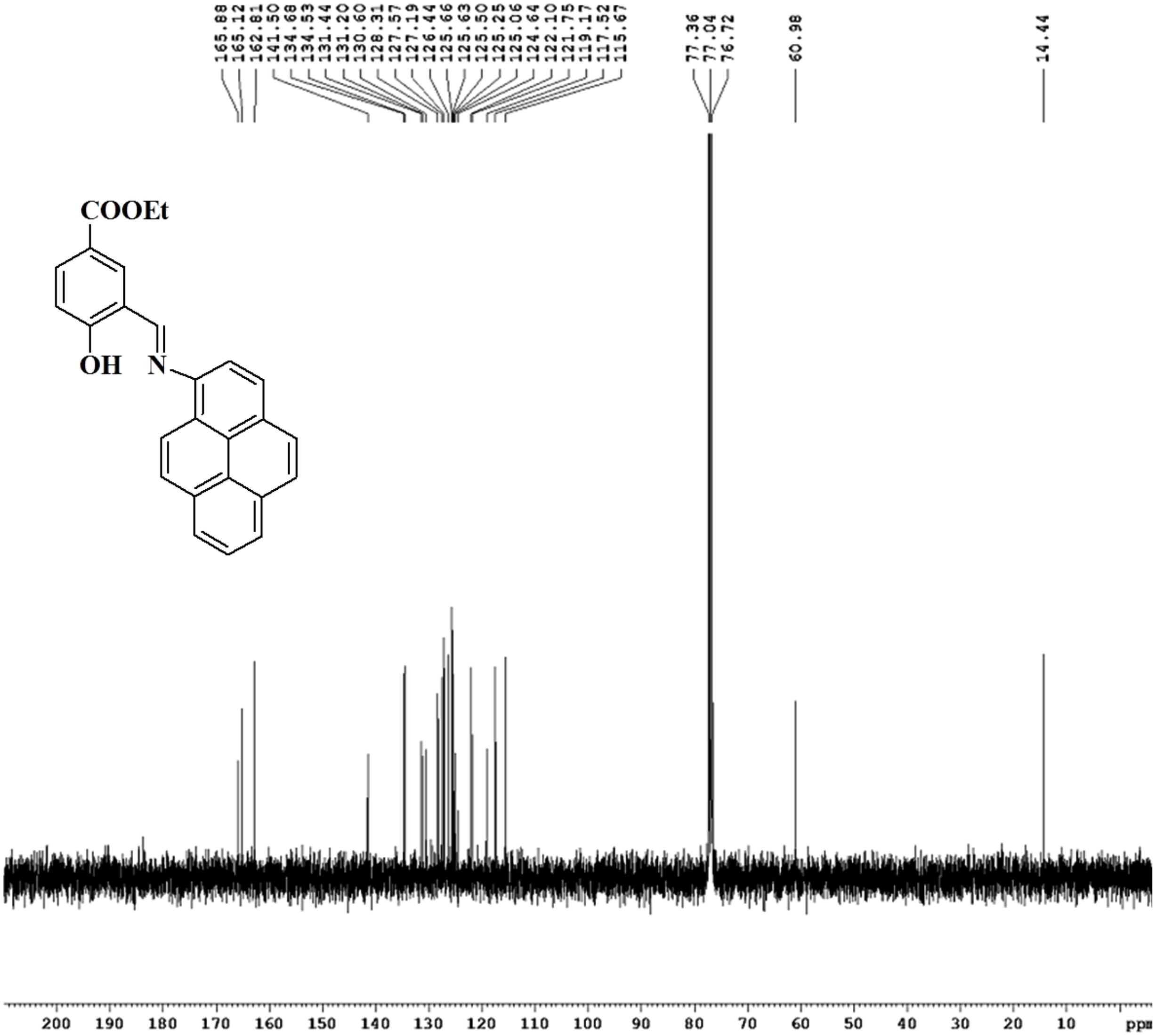
Synthesis of 3 ($C_{26}H_{19}NO_3$)

First we dissolved ethyl-3-formyl-4-hydroxybenzoate (**1**) (1mmol, 0.19 g) in 10 mL of MeOH. To this solution, 1-aminopyrene (**2**) (1mmol, 0.22 g) in 10 mL MeOH was added drop wise. The resulting solution turned from dark green to orange in color within 10 min. After 6 h, orange colored precipitates were formed which were filtered, washed with cold ethanol and dried under vacuum to get **3** in 85% yield;m.p 170^{o}C. IR(KBr, cm^{-1})υ_{max} = 1711 (C=O, ester), 1610 (C=N); ^{1}H NMR ($CDCl_{3,}$ 400 MHz): $\delta = 1.43$ [m, 3H, CH_3], 4.40 [m, 2H, CH_2], 7.15 [d, *J* = 8.0Hz, 1H, Ar-H] , 7.82 [d, *J* = 8.0 Hz, 1H, Ar-H], 8.01 - 8.27 [m, 9H, pyrene], 8.48 [d, *J* = 12.0 Hz, 1H, Ar-H], 8.92 [s, 1H, HC=N], 14.26 [s, 1H, OH]. ^{13}C NMR ($CDCl_{3,}$ 100MHz): 14.4[CH_3], 60.9[OCH_2], 115.6 [Ar-C], 117.5[Ar-C], 119.1 [Ar-C], 121.8 [Ar-C], 122.1 [Ar-C], 124.6 [Ar-C], 125.1 [Ar-C], 125.3 [Ar-C], 125.5 [Ar-C], 125.6 [Ar-C], 125.6 [Ar-C], 126.4 [Ar-C], 127.1 [Ar-C], 127.6 [Ar-C], 128.3 [Ar-C], 130.6 [Ar-C], 131.2 [Ar-C], 131.4 [Ar-C], 134.5 [Ar-C],134.6 [Ar-C], 141.5 [Ar-C], 162.8 [Ar-C], 165.1 [Ar-C], 165.9 [Ar-C=N] ppm. ESI-MS: m/z = 394.14 [M + H]$^{+}$.

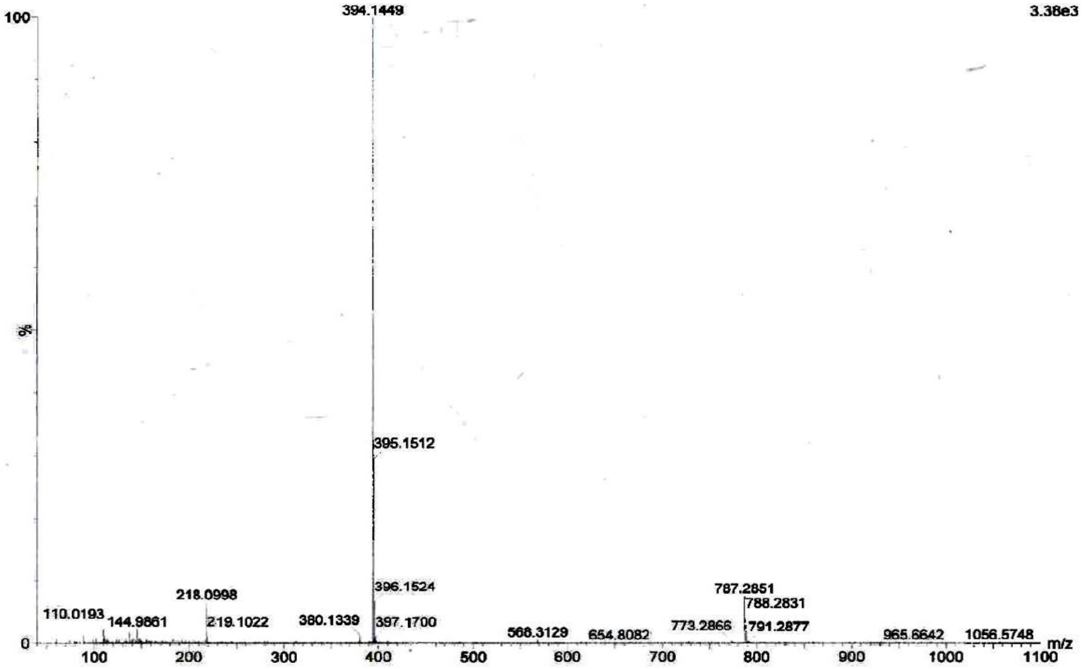
^{1}H NMR spectrum of 3



^{13}C NMR spectrum of 3



Mass spectrum of 3



The peak at m/z 394.14 corresponds to [**3**+H]$^+$

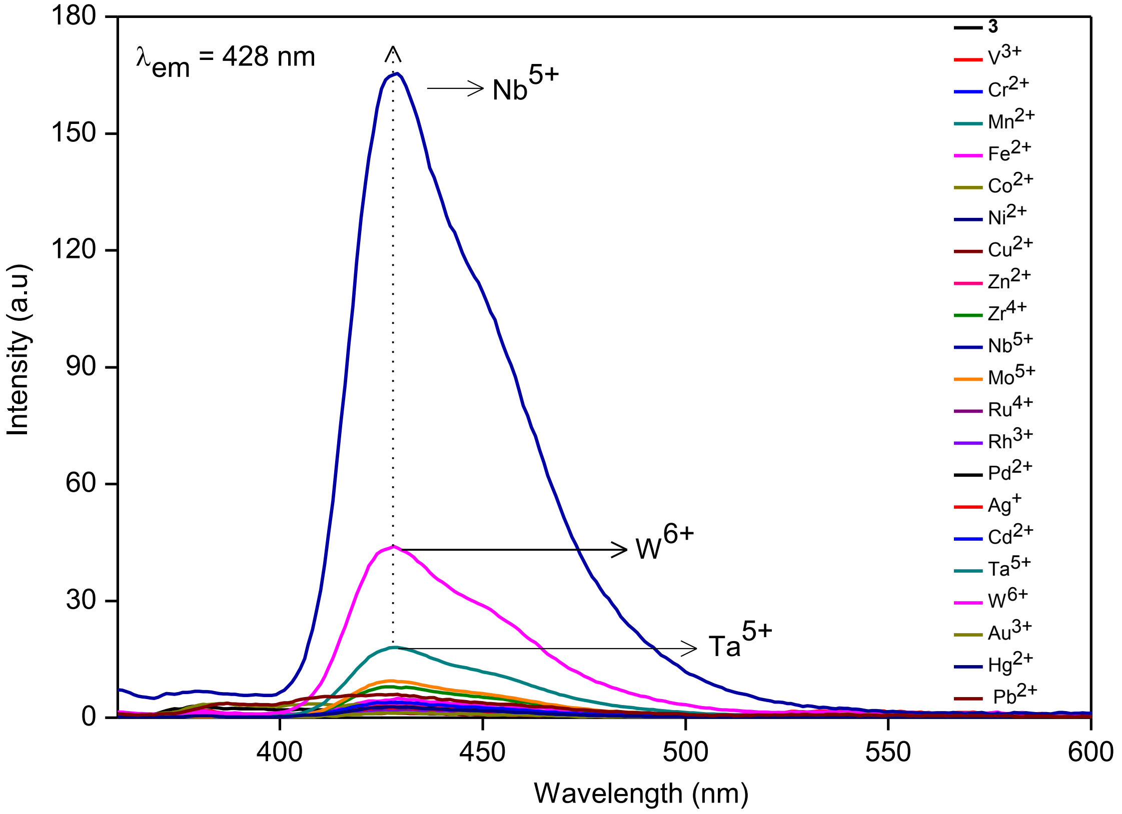
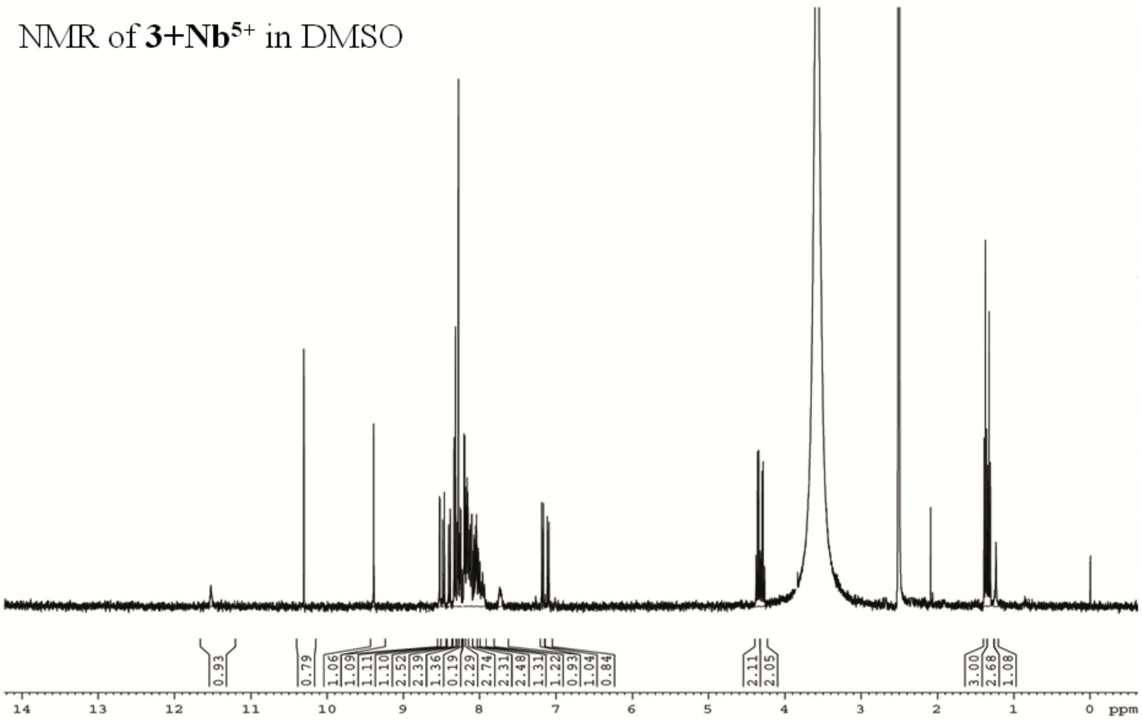
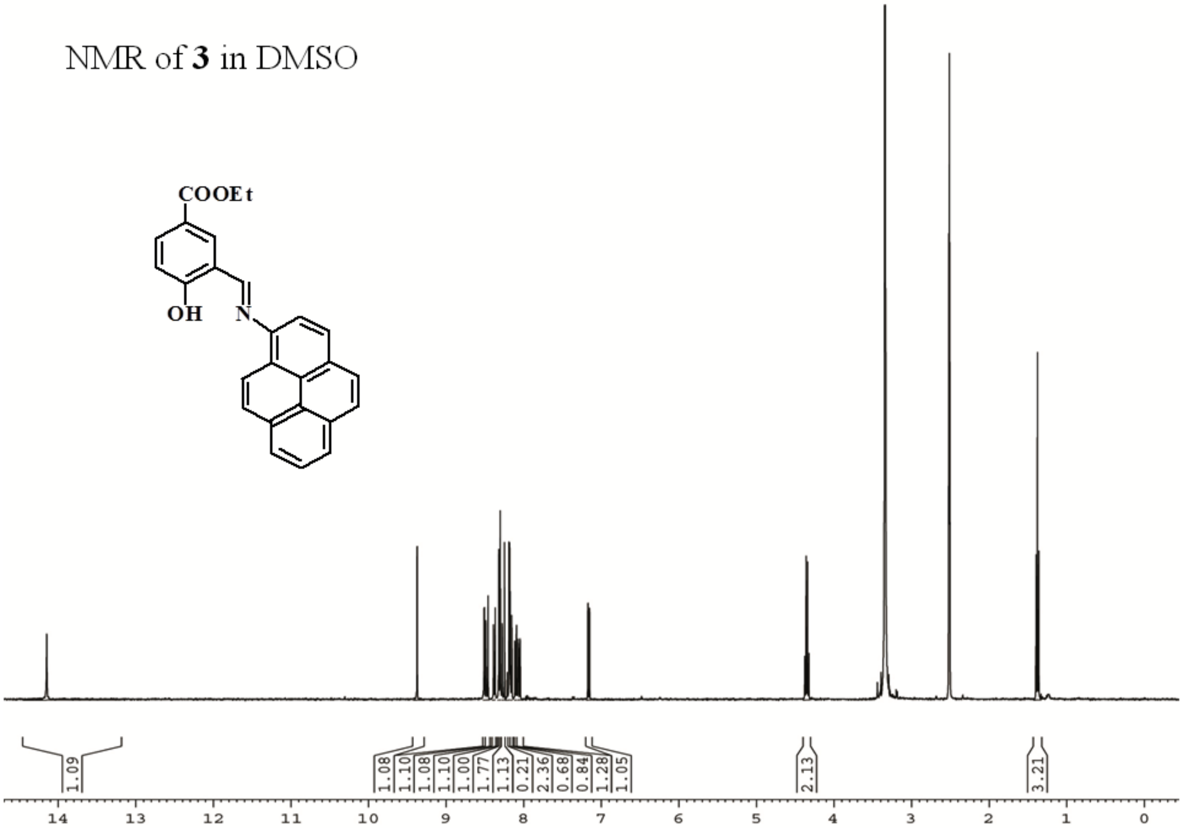
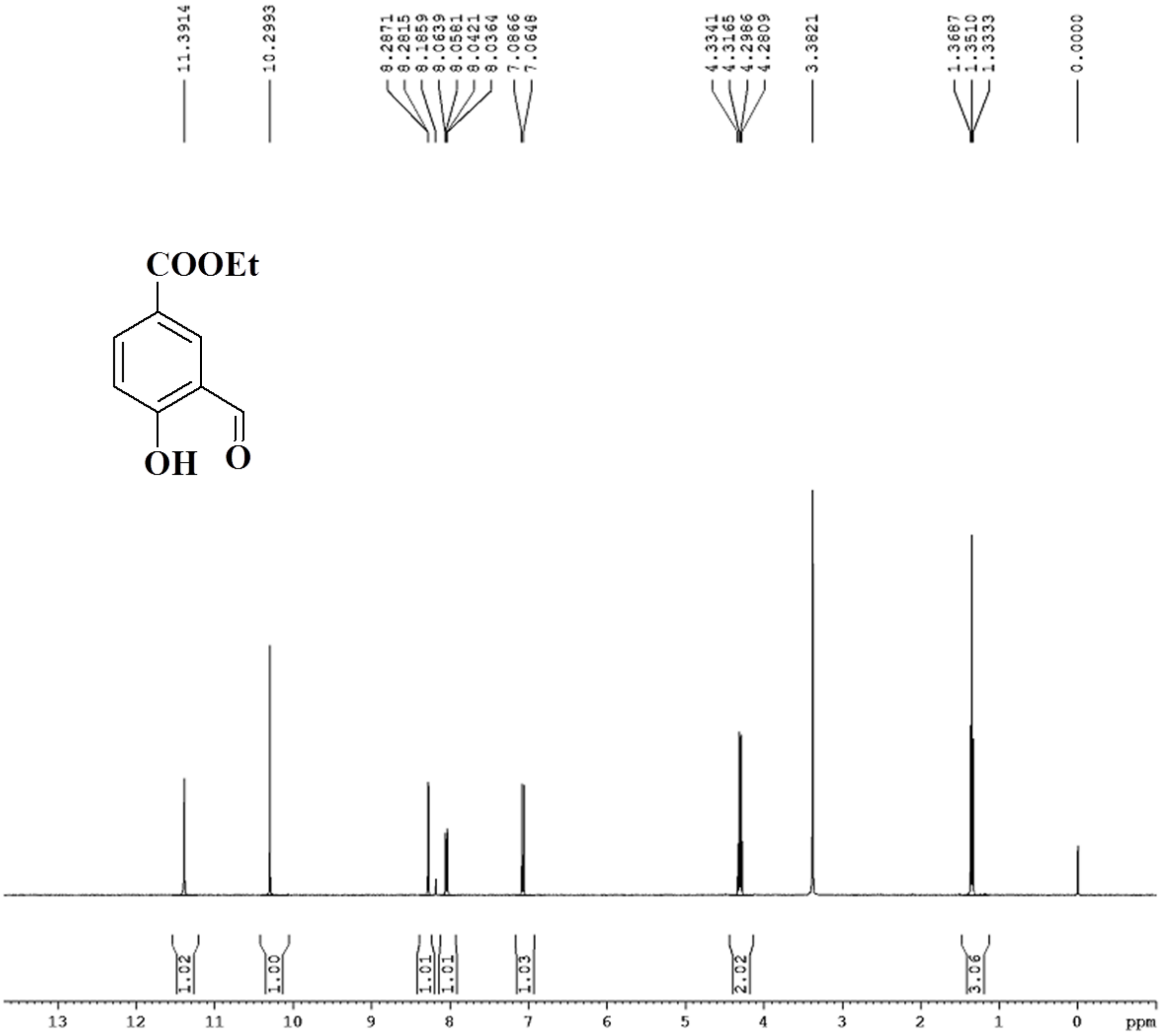


Figure S1. Fluorescence spectra of **3** (1 μM) upon addition of various metal ions (1–320 μM) in THF/H_2O (95:5, v/v) solutions, λ_{ex}= 342 nm.


NMR of **3+Nb**$^{5+}$ in DMSO


NMR of **3** in DMSO

NMR of **1** in DMSO



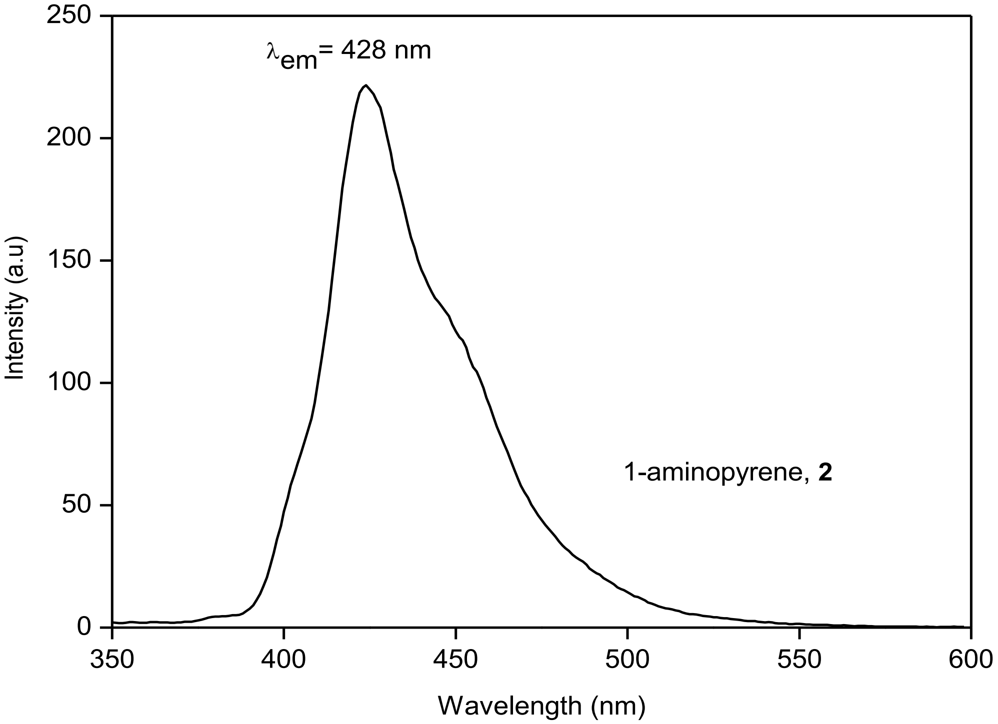
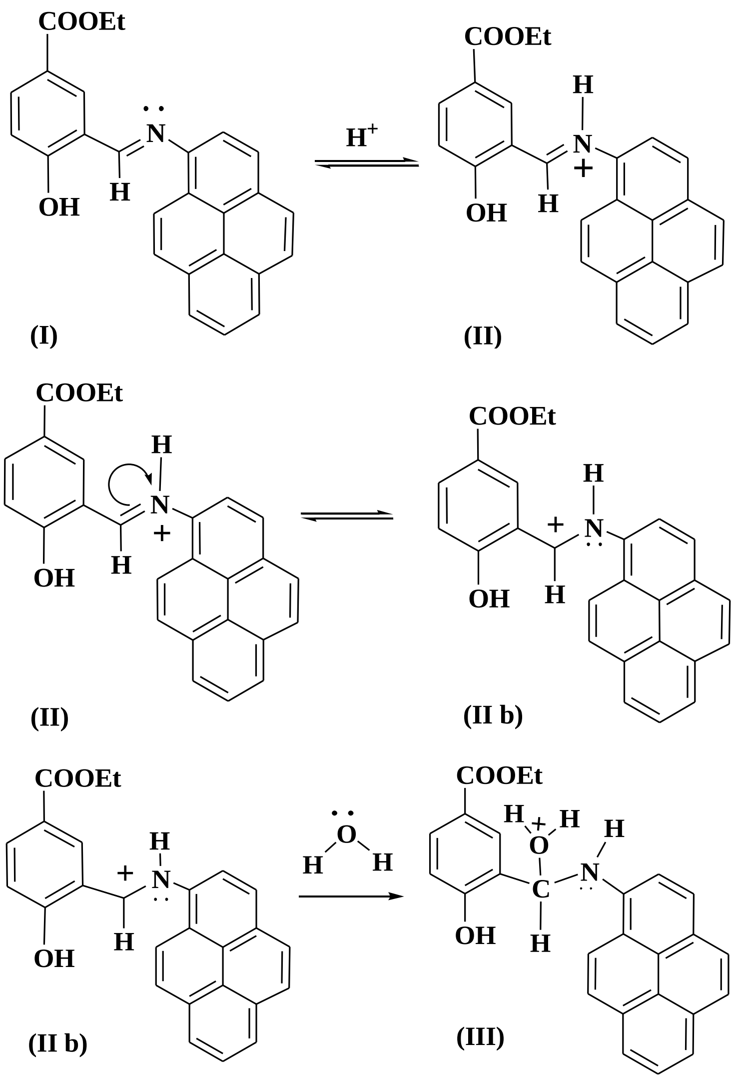


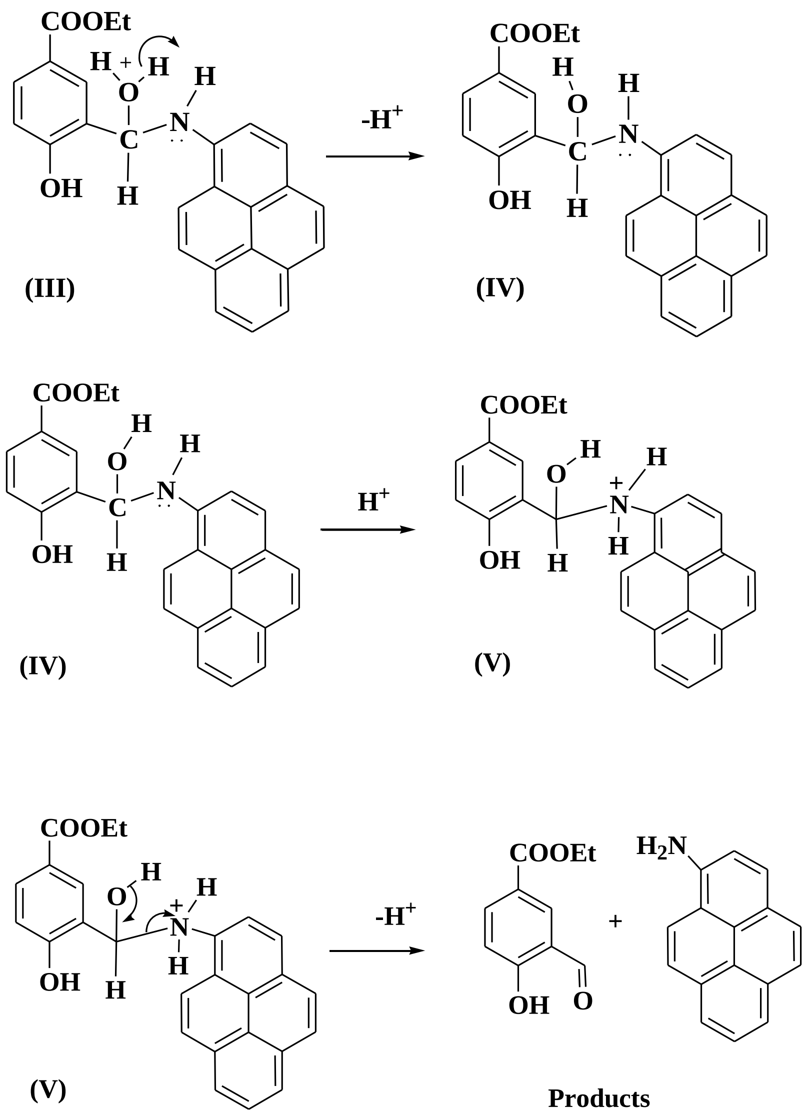
Figure S2. Fluorescence emission spectrum of 1-aminopyrene **2** (1 μM) in THF/H_2O (95:5, v/v), λ_{ex}= 342 nm.

Mechanism of acid catalyzed hydrolysis of 3

The detailed steps involved in acid catalyzed hydrolysis of imines are known.[2] Based on that, the possible steps in the case of **3** are given below.

Scheme S1



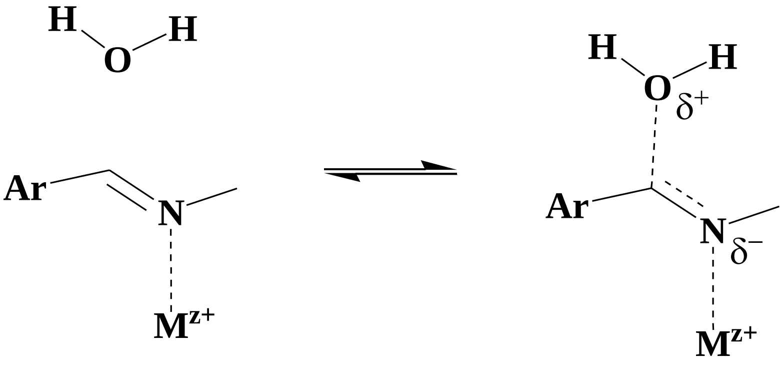


2. A. S. Kirdant, B. K. Magar and T. K. Chondhekar, *J. Chem. Bio. Phy. Sci. Sec. A*, 2011-2012, **2**, 147 – 153.

Mechanismof metal catalyzed hydrolysis of imines

The following intermediates are proposed for metal assisted hydrolysis of imines, in which an enhancement of the substrate reactivity after association with the metal ion is observed.[3]

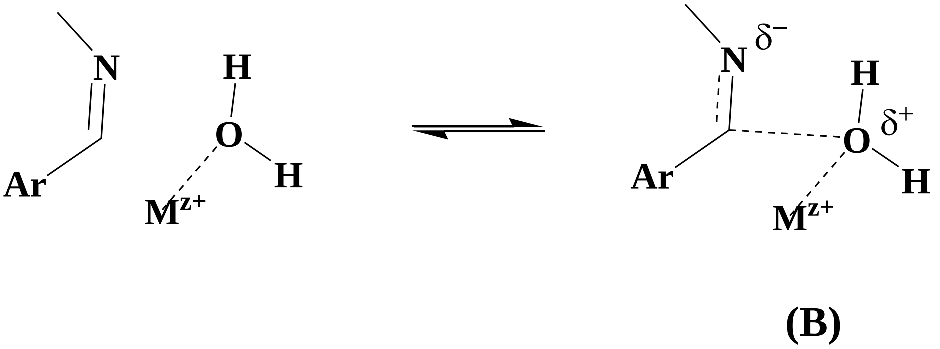
Scheme S2



(A)

In an alternate arrangement, the role of the metal ion is to activate the attacking water molecule by bringing it closer to the C=N bond as shown below.

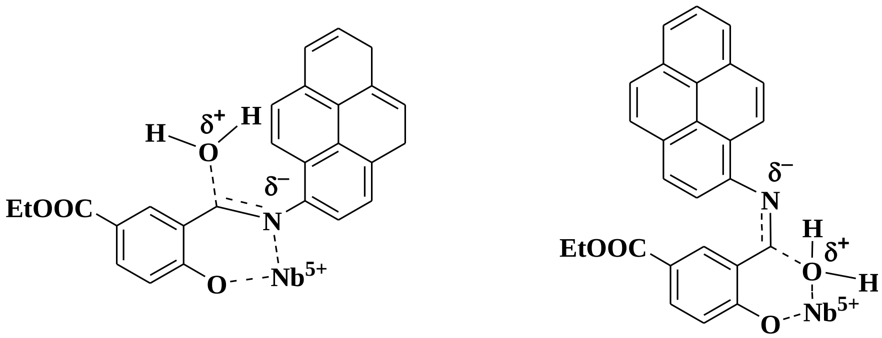
Scheme S3



(B)

For compound **3**, the intermediates **(A)** and **(B)** can be written as follows, where there will be an extra stabilization for the association of the metal ion with the substrate due to the involvement of ortho phenolic O^{-} group .

Scheme S4



(A) **(B)**

3. V. G. Machado, M. G. Nascimento and M. C. Rezende, *J. Braz. Chem. Soc.*, 1993, **4**, 76 – 79.

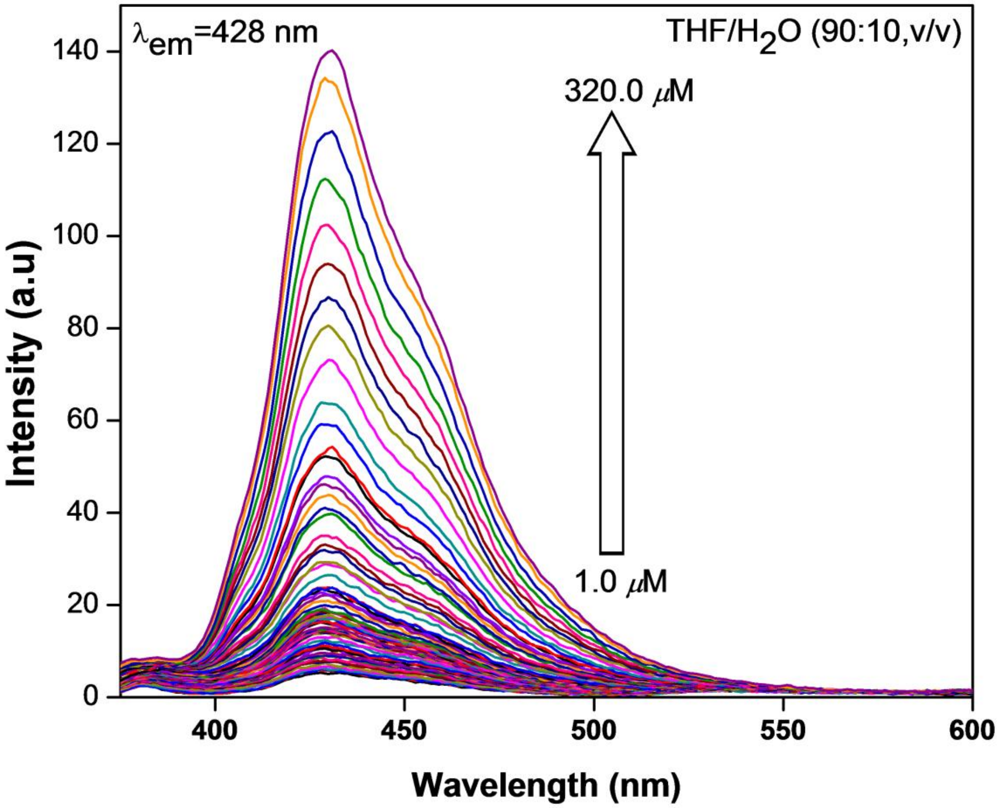


Figure S3. Spectrofluorometric titration of **3** (1 μM) with addition of Nb^{5+} (1.0-320.0 equiv) in THF/H_2O (90:10, v/v); λ_{ex}= 342 nm; buffered with HEPES.

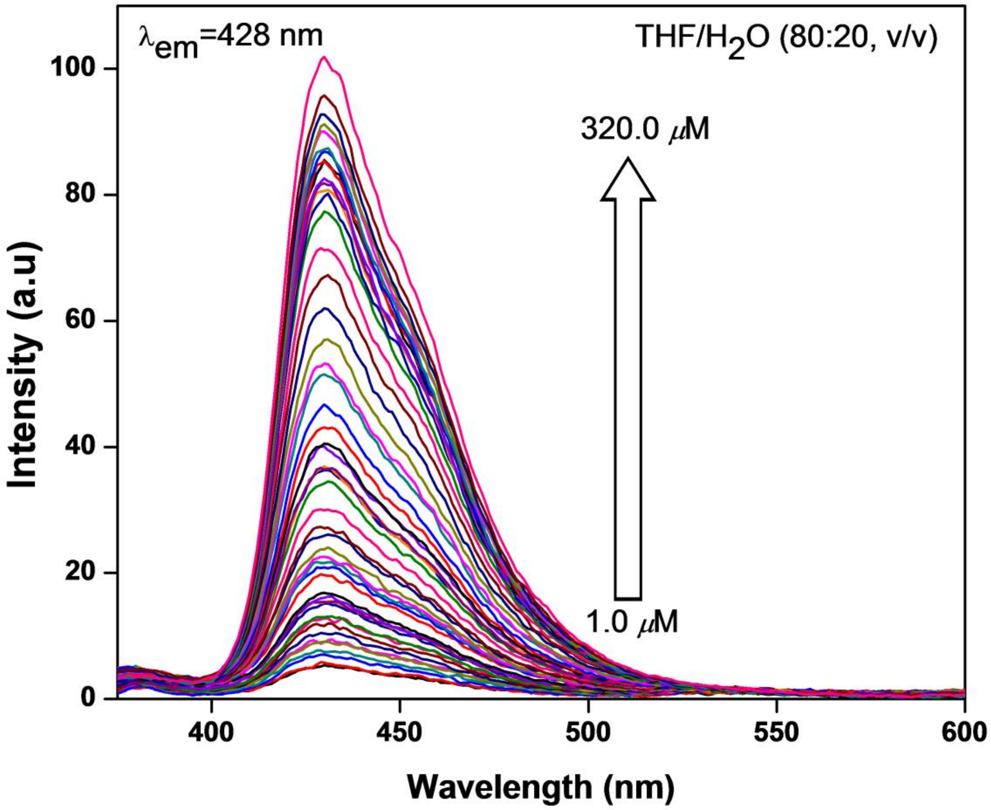


Figure S4. Spectrofluorimetric titration of **3** (1 μM) with addition of Nb^{5+} (1.0-320.0 equiv) in THF/H_2O (80:20, v/v); λ_{ex}= 342 nm; buffered with HEPES.