

Supporting Information

Pentacenequinone derivative with aggregation-induced emission enhancement characteristics for the picogram detection of Fe³⁺ ions in mixed aqueous media

Vandana Bhalla,* Ankush Gupta, and Manoj Kumar*

Department of Chemistry, UGC Sponsored-Centre for Advanced Studies-I, Guru Nanak Dev University, Amritsar-143005, Punjab, India

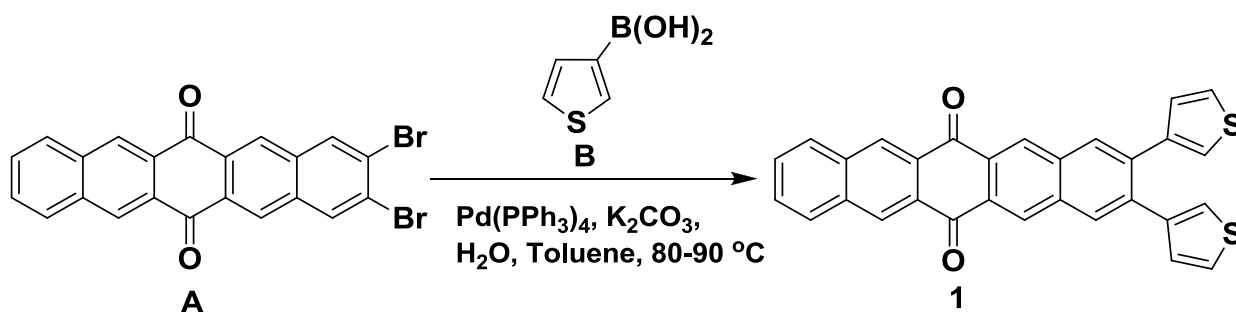
Email Address: vanmanan@yahoo.co.in

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General Experimental Procedures:

All reagents were purchased from Aldrich and were used without further purification. THF was dried over sodium and benzophenone and kept over molecular sieves overnight before use. UV-vis spectra were recorded on a SHIMADZU UV-2450 spectrophotometer, with a quartz cuvette (path length, 1 cm). The cell holder was thermostatted at 25°C. The fluorescence spectra were recorded with a SHIMADZU 5301 PC spectrofluorimeter. ^1H was recorded on a JOEL-FT NMR-AL 300 MHz spectrophotometer using CDCl_3 as solvent and tetramethylsilane SiMe_4 as internal standards. UV-vis studies were performed in THF. Data are reported as follows: chemical shifts in ppm (δ), multiplicity (s = singlet, d = doublet, br = broad singlet m = multiplet), coupling constants J (Hz), integration, and interpretation. Silica gel 60 (60–120 mesh) was used for column chromatography.

Synthetic scheme of compound 1.



Scheme 1 Pentacenequinone-based compound 1

Synthesis of compound 1. To a solution of **A** (0.5 g, 1.07 mmol) and **B** (0.302g, 2.36 mmol) in toluene were added K₂CO₃ (0.59 g, 4.28 mmol), distilled H₂O (2.1 mL), and [Pd(PPh₃)₄] (0.272 g, 0.24 mmol) under N₂, and the reaction mixture was refluxed overnight. The toluene was then removed under vacuum, and the residue so obtained was treated with water, extracted with dichloromethane, and dried over anhydrous Na₂SO₄. The organic layer was evaporated, and compound was purified by column chromatography using (70:30) (Hexane:Chloroform) as an eluent to give compound **1** in 55% yield as yellow solid; mp: >260 °C; ¹H NMR (300 MHz, CDCl₃): δ = 6.90 [d, 2H, J=6.3 Hz, ArH], 7.24-7.29 [m, 4H, ArH], 7.70-7.74 [m, 2H, ArH], 8.13-8.16 [m, 2H, ArH], 8.18 [s, 2H, ArH], 8.96 [s, 4H, ArH]; ¹³C NMR (75.45 MHz, CDCl₃): 114.27, 124.05, 125.35, 128.72, 129.52, 129.82, 130.14, 130.85, 134.46, 135.29, 137.67, 140.91, 182.93; TOF MS ES⁺: 473.2 (M+1)⁺; Elemental analysis: Calcd. for C₃₀H₁₆S₂O₂: C 76.25; H 3.41; Found: C 76.20 %; H 3.35 %.

Calculations for quantum yield¹:

Fluorescence quantum yield was determined using optically matching solutions of diphenylanthracene ($\Phi_{fr} = 0.9$ in cyclohexane) as standard at an excitation wavelength of 352 nm and quantum yield is calculated using the equation:

$$\Phi_{fs} = \Phi_{fr} \times \frac{1 - 10^{-A_r L_r}}{1 - 10^{-A_s L_s}} \times \frac{N_s^2}{N_r^2} \times \frac{D_s}{D_r}$$

Φ_{fs} and Φ_{fr} are the radiative quantum yields of sample and the reference respectively, A_s and A_r are the absorbance of the sample and the reference respectively, D_s and D_r the respective areas of emission for sample and reference. L_s and L_r are the lengths of the absorption cells of sample and reference respectively. N_s and N_r are the refractive indices of the sample and reference solutions (pure solvents were assumed respectively).

¹ J. N. Demas and G. A. Grosby, *J. Phys. Chem.*, 1971, **75**, 991.

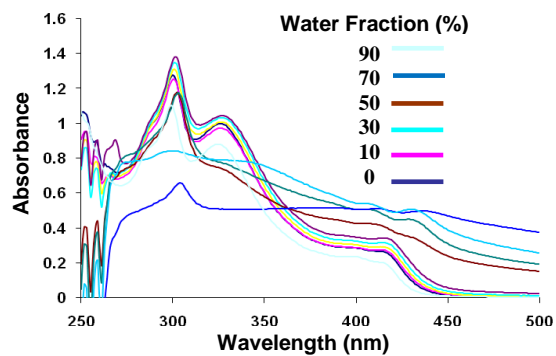


Fig. S1. Absorption spectra of compound **1** (10 μM) showing the variation of absorption intensity in H₂O/THF mixture with different water fractions.

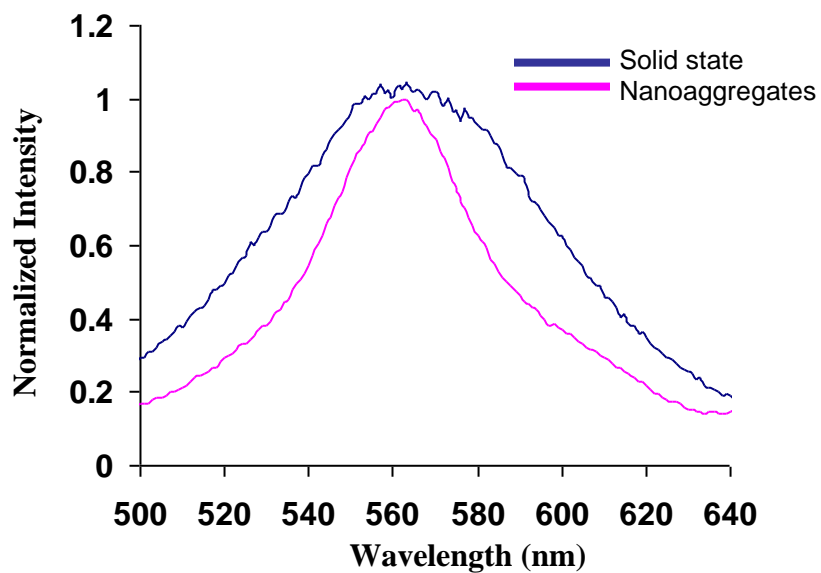


Fig. S2. Normalized fluorescence spectra of nanoaggregates and solid state spectra of compound **1**.

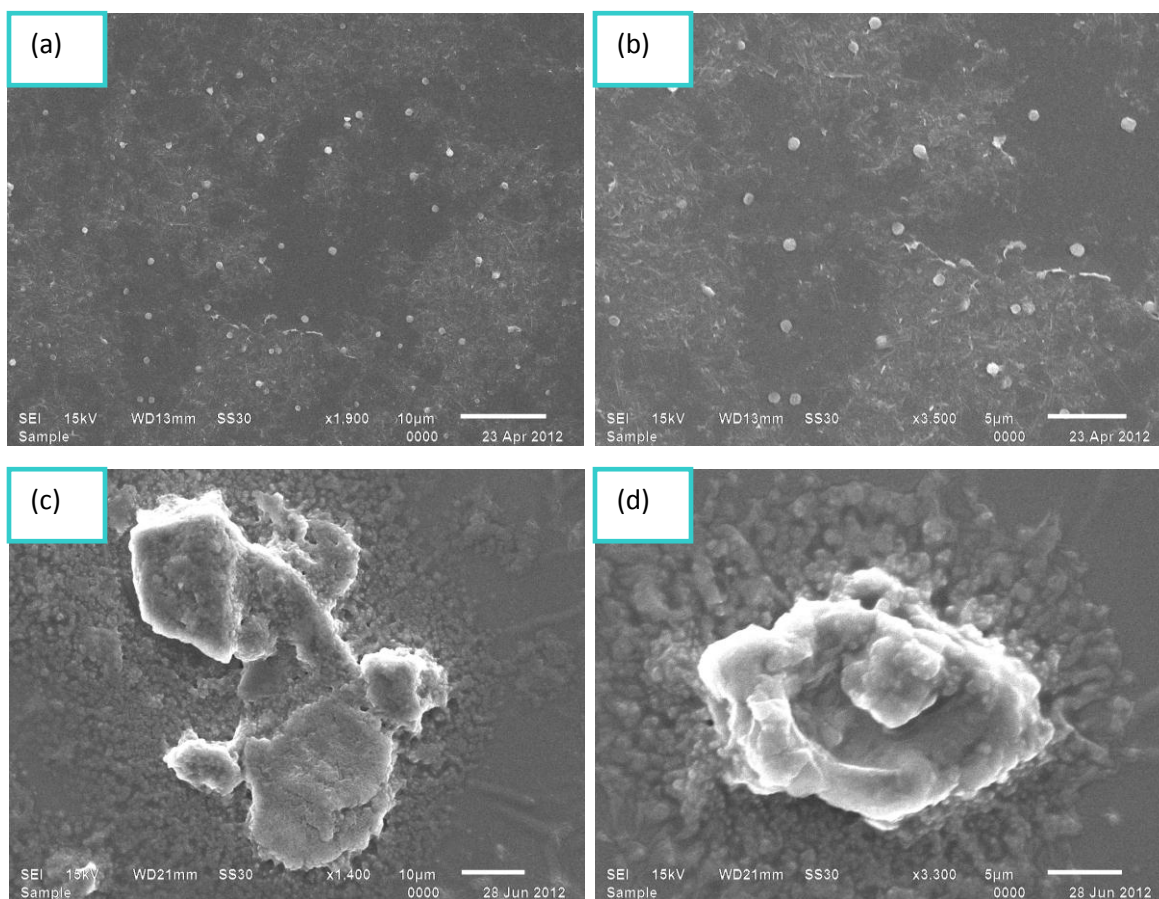


Fig. S3 (a) and (b) are SEM images of **1** nanoaggregates obtained from a suspension that contained 90% volume fraction of water in THF. (c) and (d) are larger aggregates of **1.Fe³⁺** complex. scale bar (a and c) 10 µm (b and d) 5 µm.

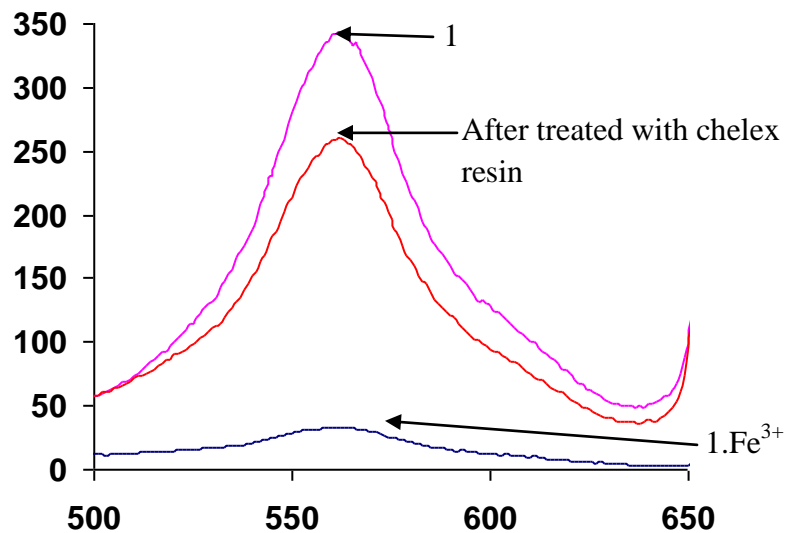


Fig. S4A Fluorescence spectra of compound **1** (10.0 μM) upon additions of 210 equiv. of Fe^{3+} ions in $\text{H}_2\text{O}/\text{THF}$ (9:1) mixture buffered with HEPES, pH = 7.0, and treated with chelex resin after the addition of 210 equiv. of Fe^{3+} ions.

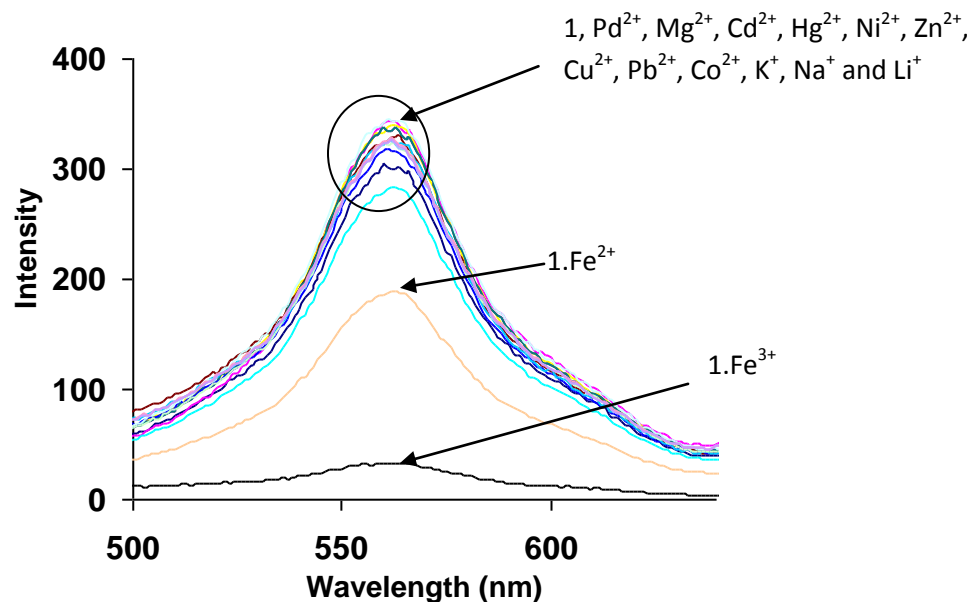


Fig. S4B Fluorescence spectra of compound **1** (10.0 μM) upon additions of 210 equiv. of various metal ions in $\text{H}_2\text{O}/\text{THF}$ (9:1) mixture buffered with HEPES, pH = 7.0

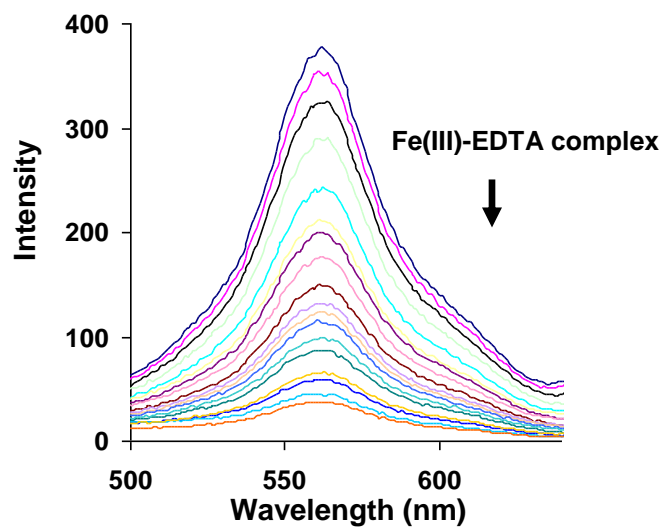


Fig. S5 Fluorescence spectra of compound **1** ($10.0 \mu\text{M}$) upon additions of 230 equiv. of Fe(III)-EDTA complex in $\text{H}_2\text{O}/\text{THF}$ (9:1) mixture buffered with HEPES, $\text{pH} = 7.0$

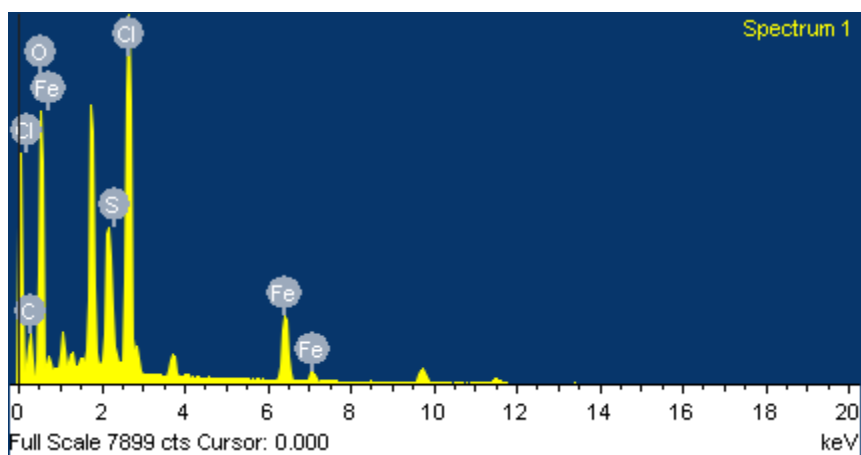


Fig. S6 SEM-EDX spectrum of nanoaggregates of **1** in presence of Fe^{3+} ions

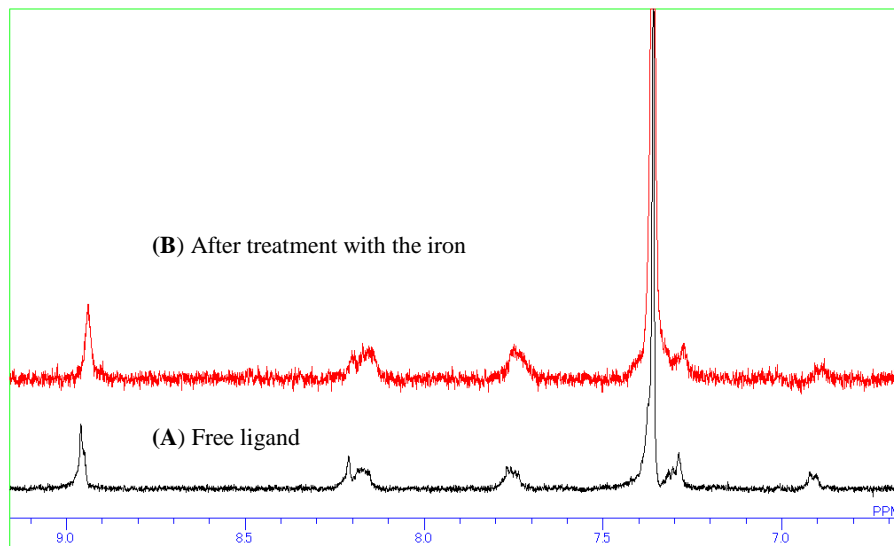


Fig. S7 ^1H NMR spectra of **1** in $\text{CDCl}_3/\text{CD}_3\text{CN}$ (8:2). (A) Free ligand (B) after treatment with the iron perchlorate (iron ions has been removed before NMR studies using chelex resin)²

² (a) D. Y. Lee and H. C. Zheng, *Plant Soil*, 1994, **164**, 19; (b) M. H. Kim, H. H. Jang, S. Yi, S. K. Chang and M. S. Han, *Chem. Commun.*, 2009, 4838.

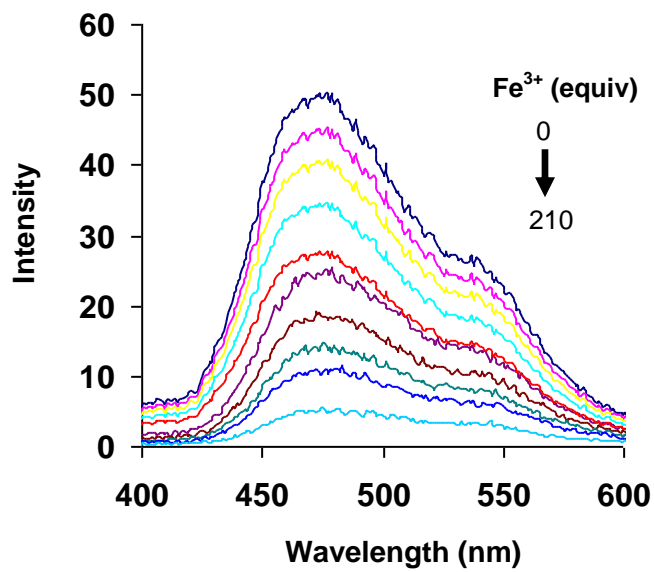


Fig. S8 Change in fluorescence spectrum of compound **1** (10 μM) with the addition of Fe^{3+} ions in THF

^1H NMR of compound **1** in CDCl_3

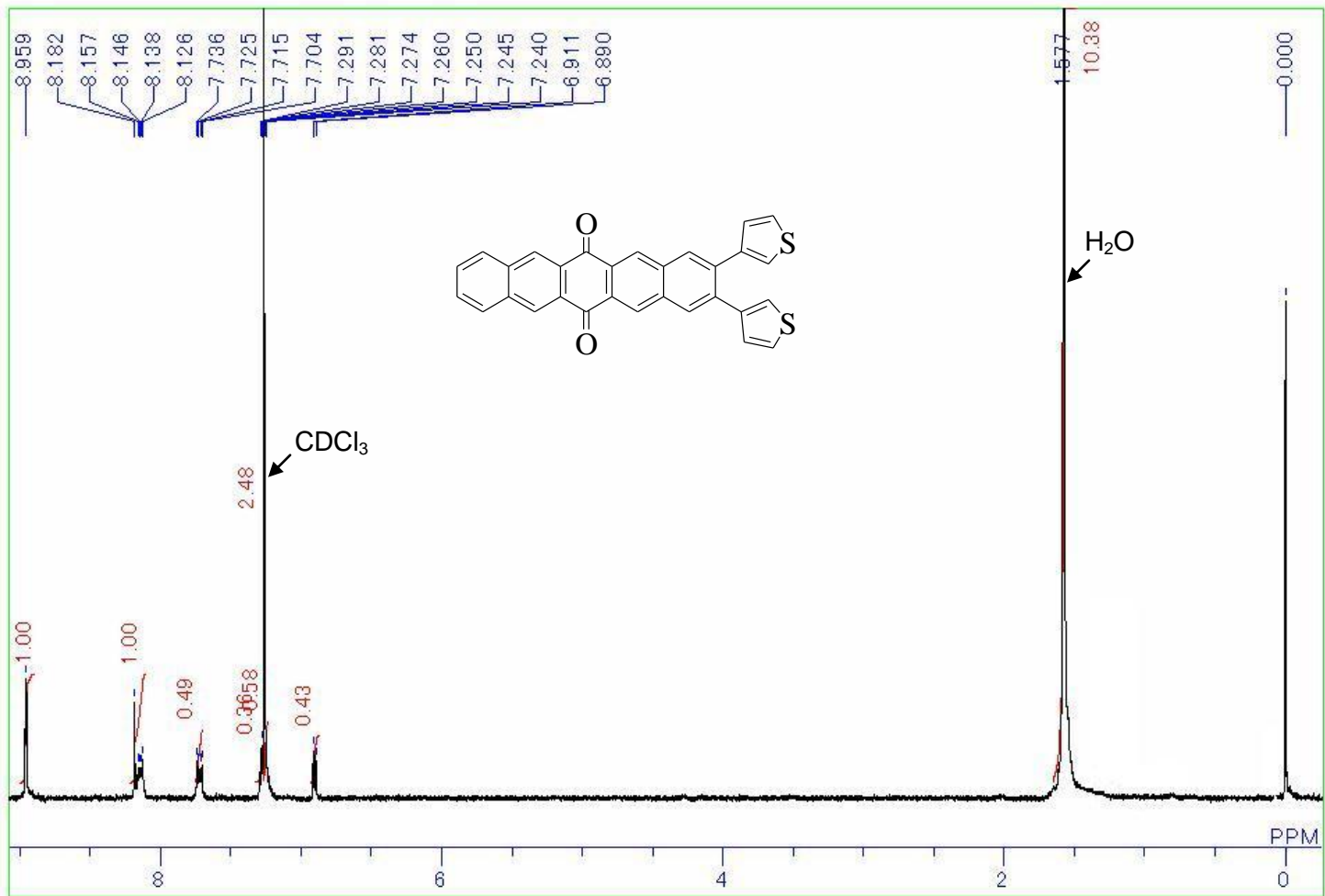


Figure S9 ^1H NMR spectrum of compound **1**

^{13}C NMR of compound **1** in CDCl_3

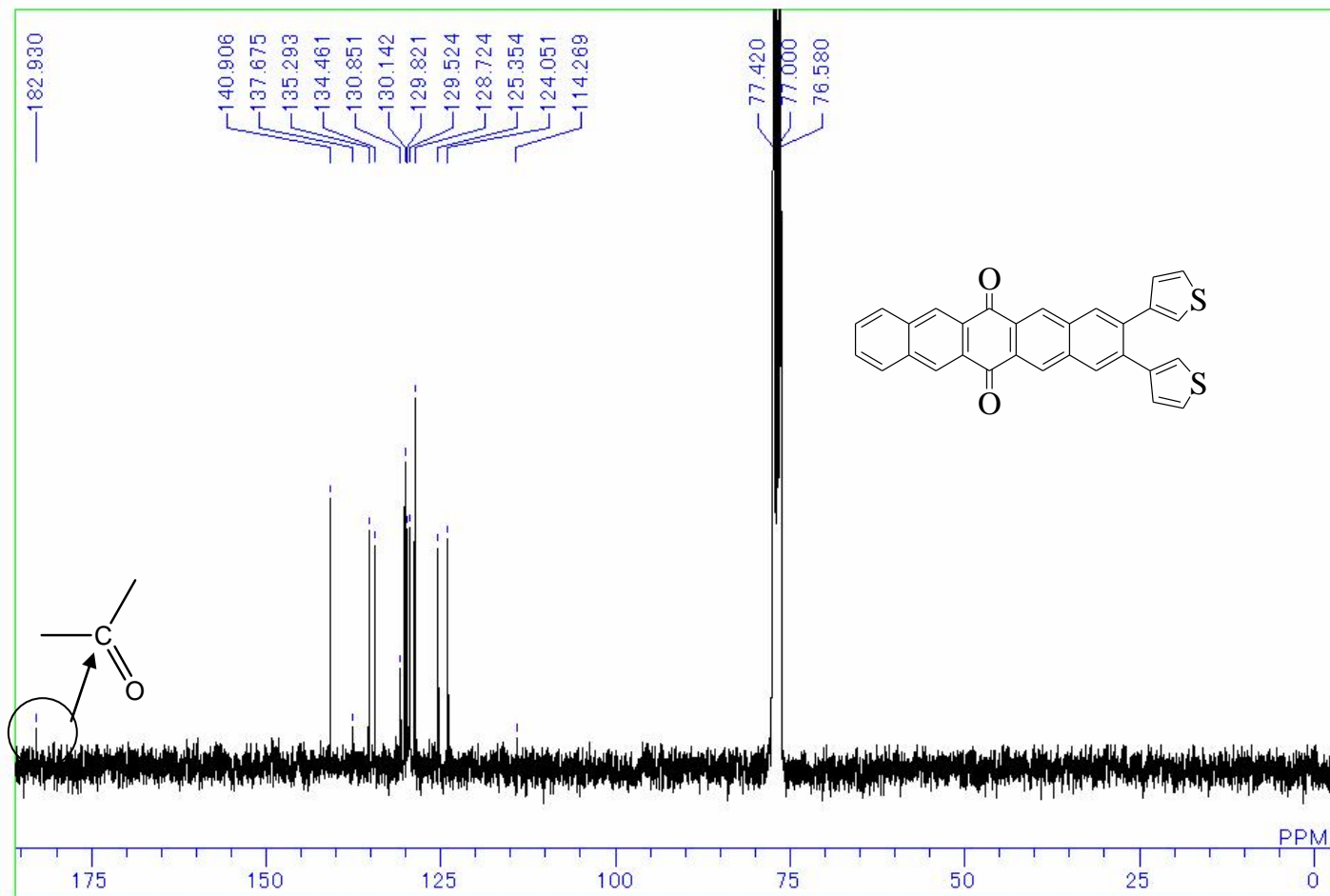


Figure S10 ^{13}C NMR spectrum of compound **1**.

Mass spectrum of compound 1

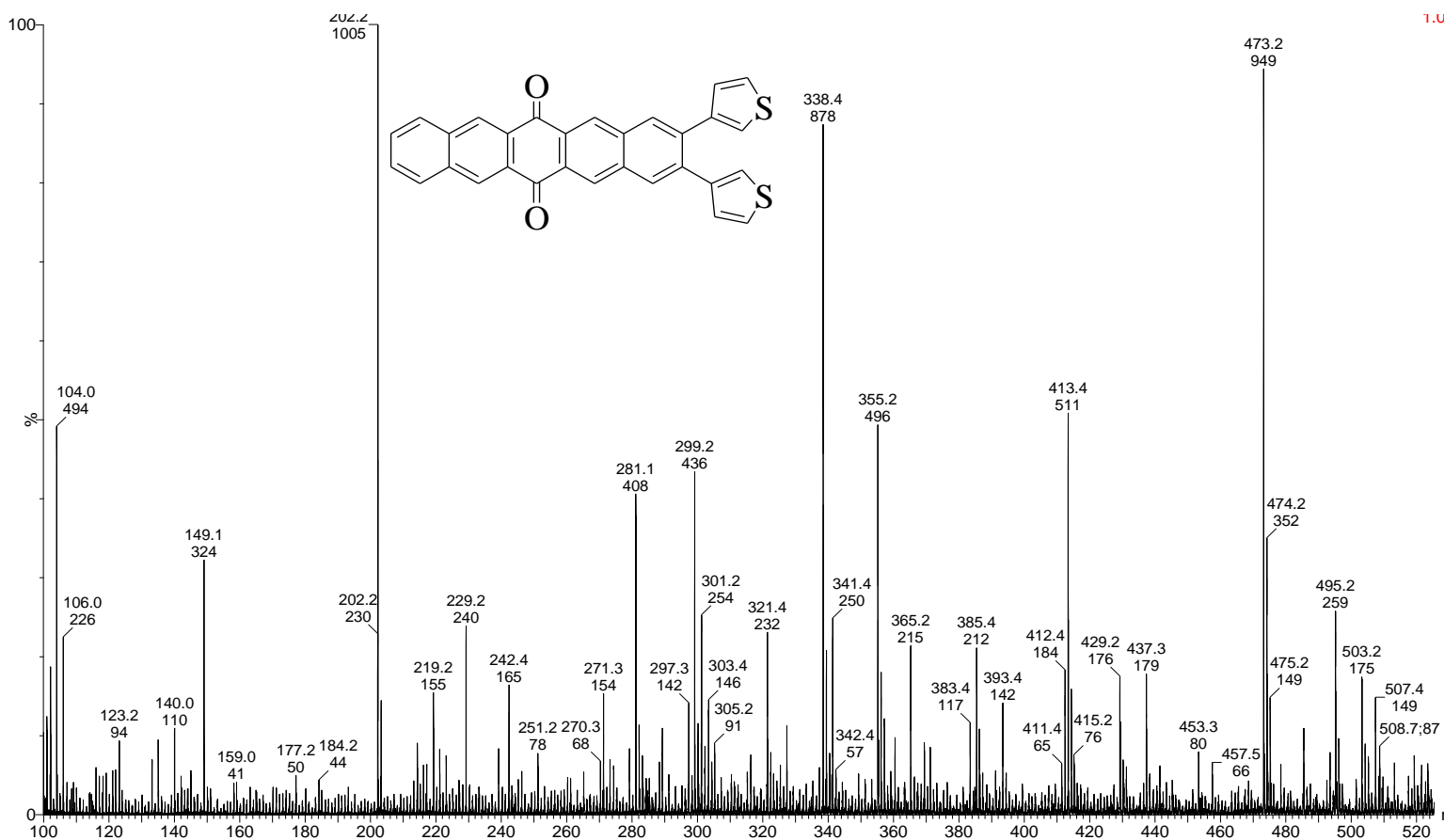


Figure S11 Mass spectrum of compound 1