Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
This journal is © The Royal Society of Chemistry 2013

Supplementary Information

for

A highly selective chemodosimeter for fast detection and intracellular imaging of Hg^{2+} ions based on a dithiocarbamate-isothiocyanate conversion in aqueous ethanol

*Suman Pal, Joydev Hatai, Mousumi Samanta, Alok Shaurya, and Subhajit Bandyopadhyay**

Department of Chemical Sciences
Indian Institute of Science Education and Research Kolkata (IISER Kolkata)
Nadia, WB 741252, India

sb1@iiserkol.ac.in

Contents

General information

The structures of the compounds were determined by 1D and 2D nuclear magnetic resonance spectroscopy and other spectroscopic and spectrometric techniques. ^{1}H and ^{13}C NMR spectra were recorded with 400 MHz Jeol and 500 MHz Bruker instruments. Chemical shifts are reported in δ values relative to an internal reference of tetramethylsilane (TMS) or the solvent peaks. IR data were obtained with a Perkin-Elmer-spectrum-100 spectrophotometer. Mass spectrometry data were obtained from Waters Acuity Ultra Performance LC. Emission spectra were recorded in Horiba Jobin Yvon (Fluoromax-3). UV absorption spectra were recorded in Varian Cary 300 Bio spectrophotometer. Fluorescence imaging experiments were carried out using an Olympus IX 51 inverted microscope with UV excitation. pH data were recorded with a Sartorius Basic Meter PB-11 calibrated at pH 4, 7, and 10. Solvents used were purified and dried by standard methods. Reactions were monitored by thin layer chromatography using Merck plates (TLC Silica Gel 60 F_{254}). Developed TLC plates were visualized with UV light (254 and 366 nm). Silica gel (100−200 mesh, Merck) was used for column chromatography. Yields indicate the chromatographically and spectroscopically pure compounds. The solvents used for the spectroscopy experiments were of the spectroscopic grades and were free from any fluorescent impurity. Milli-Q ultrapure water was used for the experiments.

Crystal Data were collected on a Bruker SMART APEXII CCD area-detector diffractometer using graphite monochromated Mo Kα radiation (λ= 0.71073 Å). For both thecrystals, X-ray data reduction was carried out using the Bruker SAINT program. The structures were solved by direct methods using the SHELXS-97 program and refinement using SHELXL-97 program. Selected crystal data and data collection parameters are given in Table 1. X-ray data reduction, structure solution and refinement were done using the SHELXL-97 program package.

The solutions of metal ions were prepared with $Al(NO_3)_3 \cdot 9H2O$, $LiClO_4 \cdot 3H_2O$, $NaClO_4$, $KClO_4$, $Ba(NO_3)_2 \cdot 4H_2O$, $Mn(ClO_4)_2$, $Fe(ClO_4)_2 \cdot xH_2O$, $Co(ClO_4)_2 \cdot 6H_2O$, $Cr(ClO_4)_3 \cdot 6H_2O$, $Cd(NO_3)_2$, $AgNO_3$, $Hg(NO_3)_2$, $Pb(ClO_4)_2$, $Ca(ClO_4)_2 \cdot 4H_2O$, $Cu(ClO_4)_2.6H_2O$, $Ni(ClO_4)$, and $Zn(ClO_4)_2 \cdot 6H_2O$ for the respective metal ions.

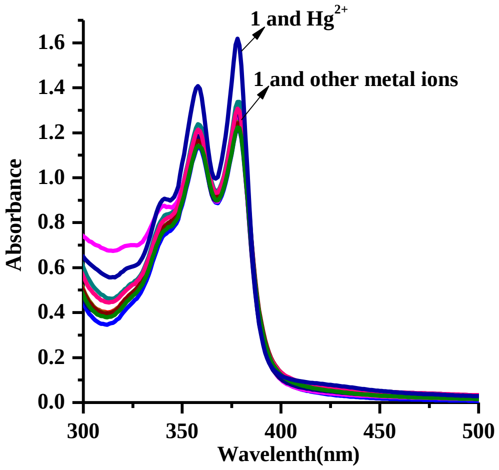

Figure S1. Absorption spectra of **1**(10 µM) upon addition of various metal ions (20 µM) in mixed solvent media (H_2O/EtOH, 4:1, v/v, with 1% DMSO as a cosolvent, 1 mM HEPES buffered at pH 7.0) at 25 ^{o}C.

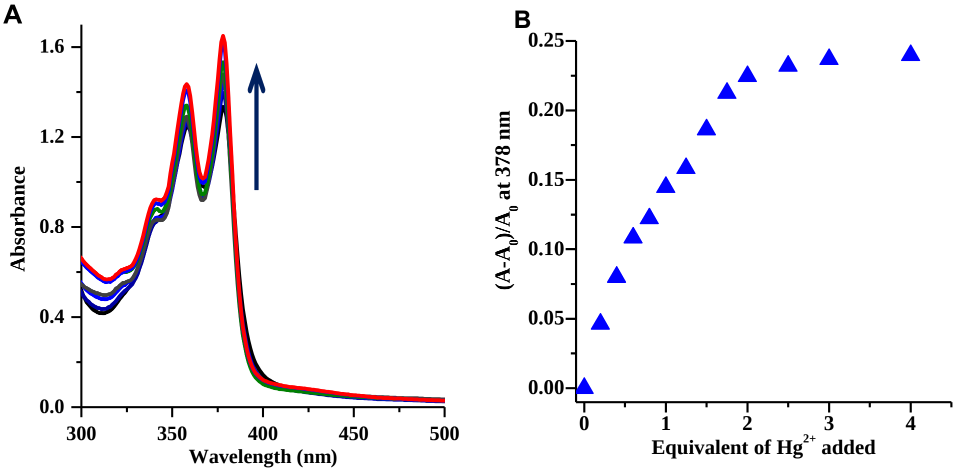

Figure S2. (A) Change in the absorption spectra of **1** (10 µM) with the addition of various equivalent of Hg^{2+} (0 to 50 µM) in mixed solvent media (H_2O/EtOH, 4:1, v/v, with 1% DMSO as a cosolvent, 1 mM HEPES buffered at pH 7.0); (B) Hg^{2+} titration profile at 378 nm in mixed solvent media.

Detection limit

The detection limit for the Hg^{2+} ions were calculated based on the fluorescence titration experiments. To determine the S/N ratio, the fluorescence intensity of the blank (**1** (10 µM) in absence of Hg^{2+}) was recorded 10 times in mixed solvent media (H_2O/EtOH, 4:1, v/v, with 1% DMSO as a cosolvent, 1 mM HEPES buffered at pH 7.0) and the standard deviation of the blank measurements was determined. Under the same conditions, the fluorescence spectra of dosimeter **1** (10 µM) was recorded in presence of Hg^{2+} (0 to 50 µM). A linear curve (0 – 15 µM, $R^2 = 0.98$, figure S3) was obtained when fluorescence intensity was plotted against the concentration of Hg^{2+}. The detection limit thus calculated was found to be 2.1×10^{-7} (M).

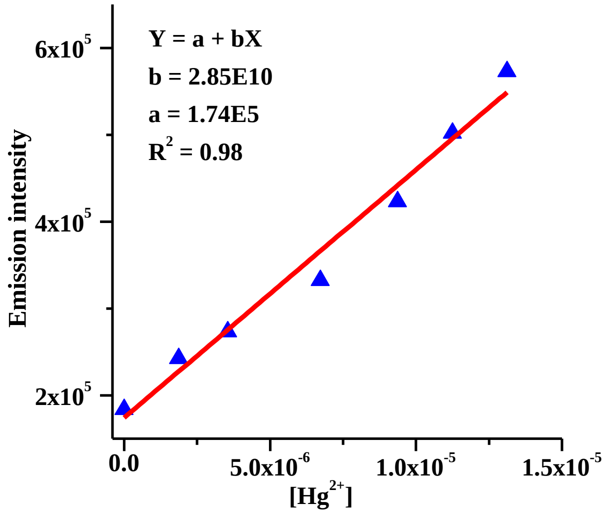

Figure S3. Determination of the detection limit of Hg^{2+} with **1** (10 µM) at 409 nm.

Determination of quantum yield

Relative quantum yield was calculated from the equation stated below:

$$\Phi_F = \Phi_S \frac{A_S}{A_U} \frac{F_U}{F_S} \frac{\eta_U^2}{\eta_S^2}$$

Where ϕ_S is the quantum yield of the standard, A is the absorbance at the excitation wavelength (subscript S for standard*and U for unknown), F is the area under the emission spectra and η is the refractive index of the solvent.[1]

**Quinine sulphate was used as reference.*

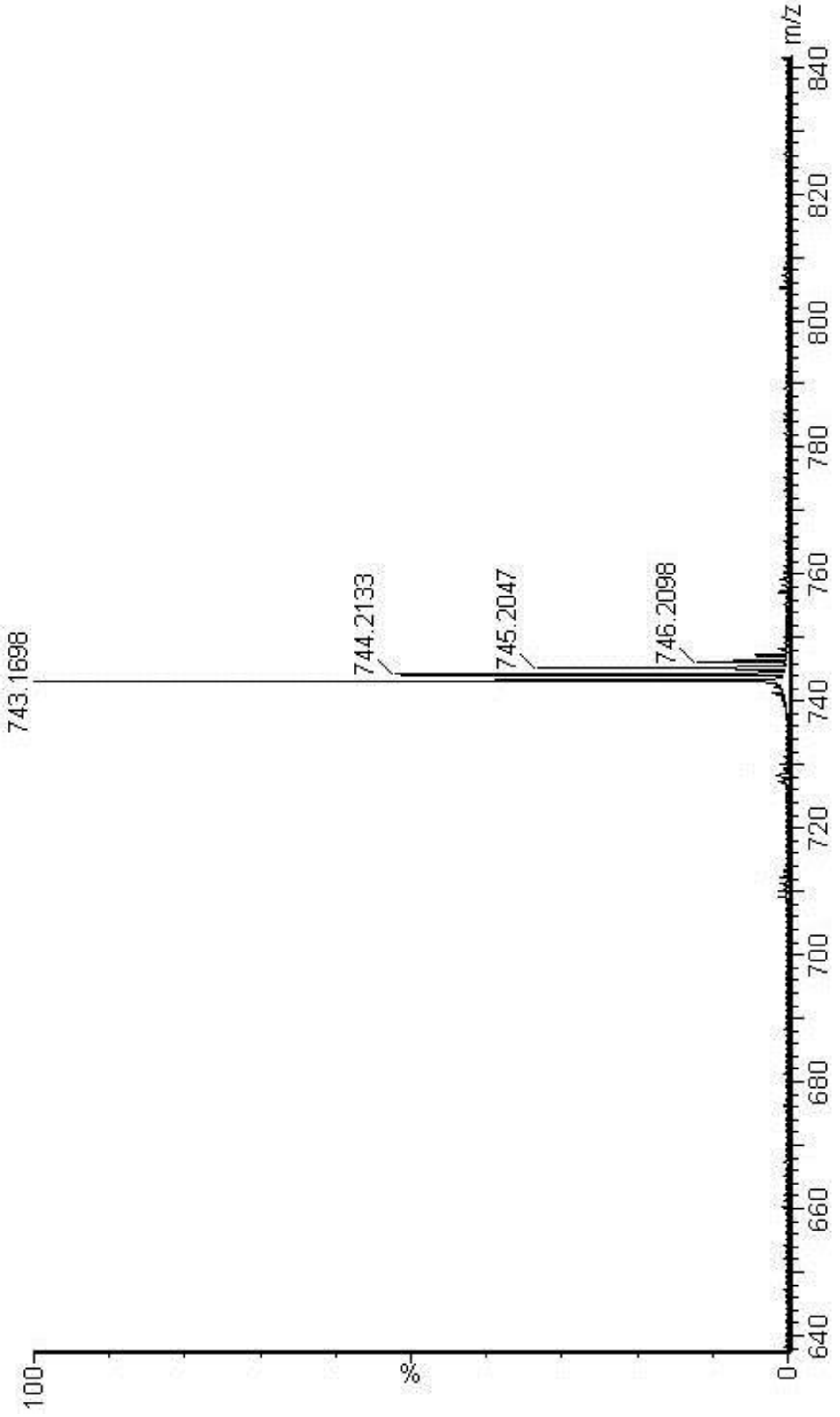

Figure S4. Mass spectrum of **1**.

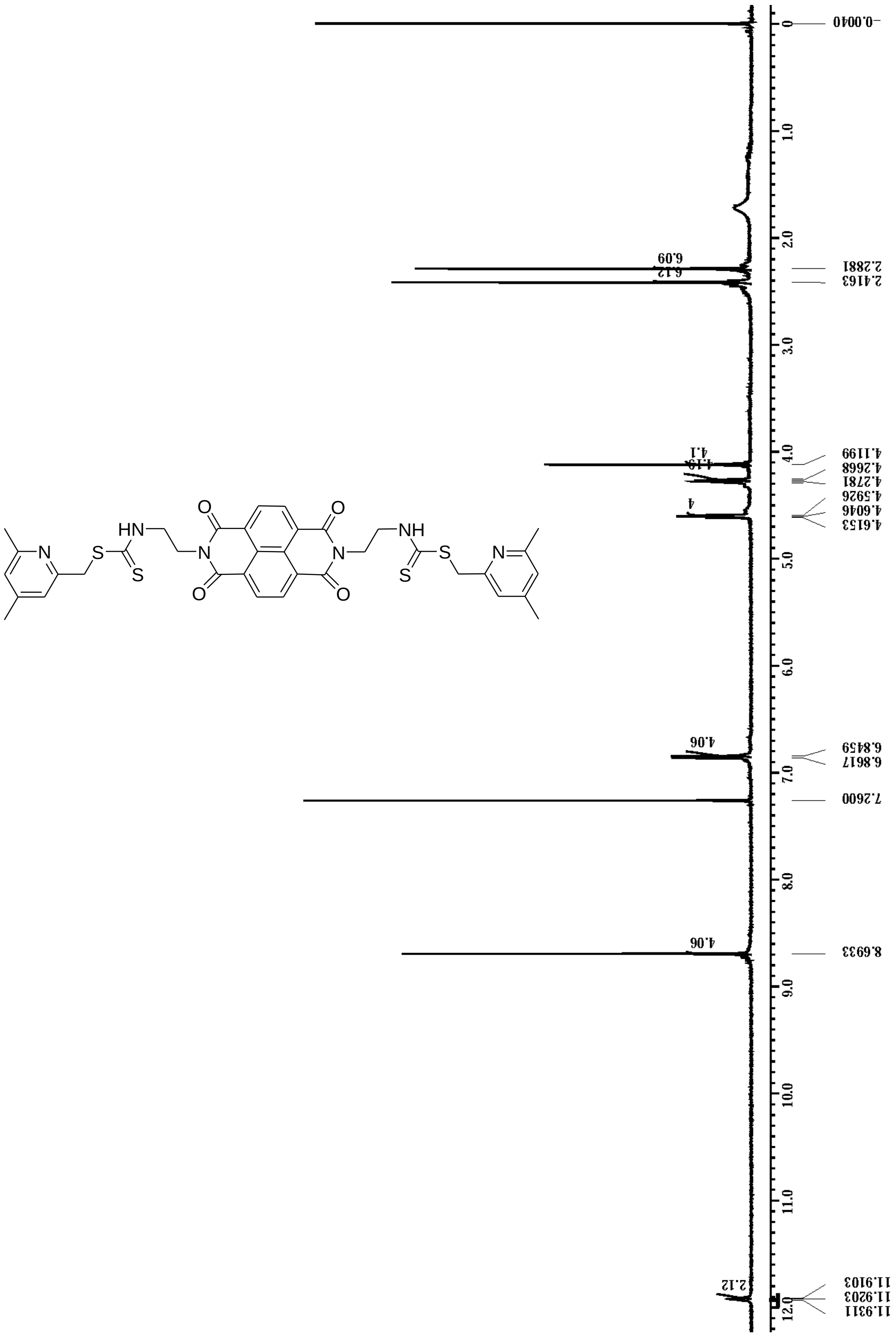

Figure S5. ^{1}H NMR spectrum of **1**.

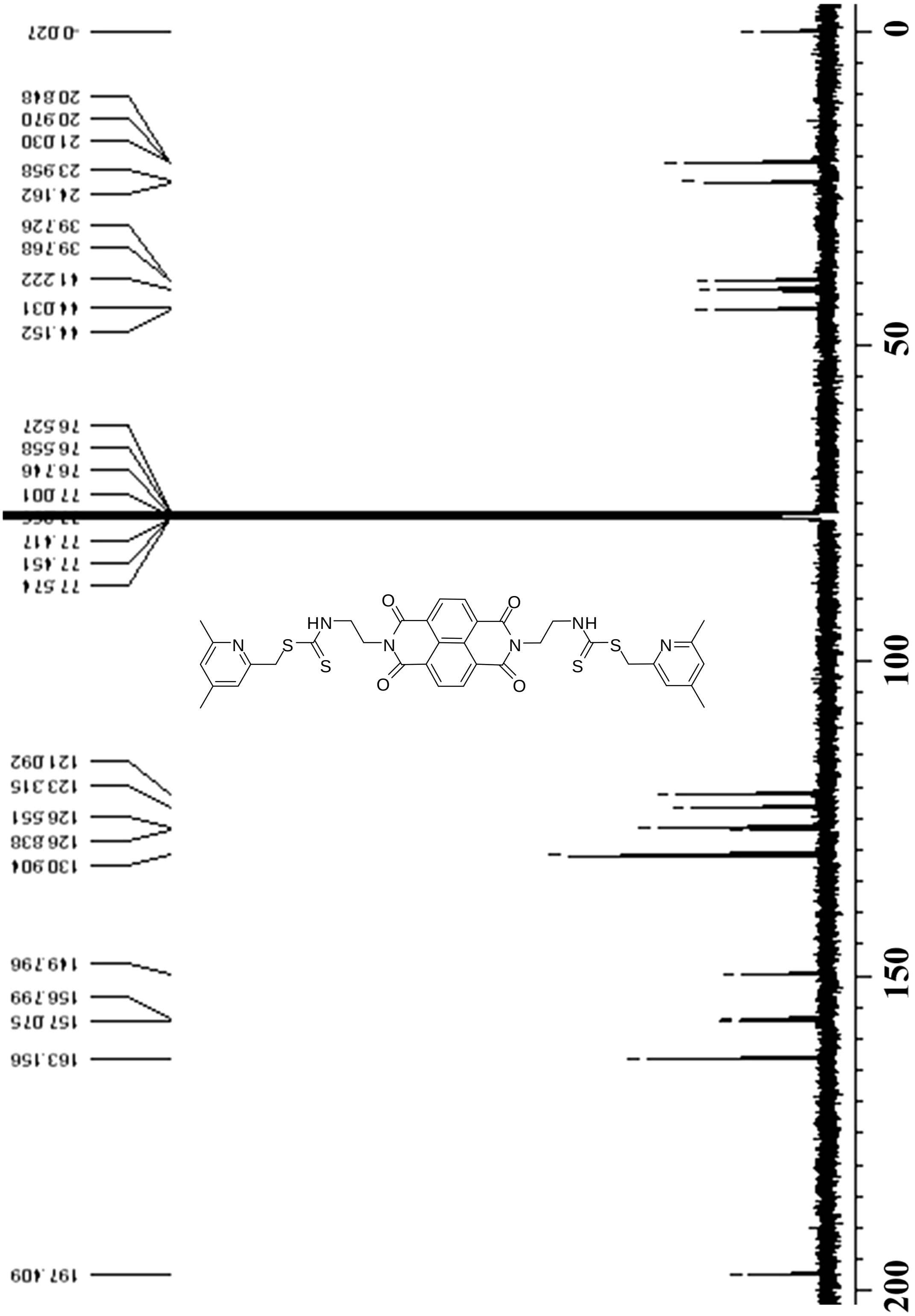

Figure S6. ^{13}C NMR spectrum of **1**.

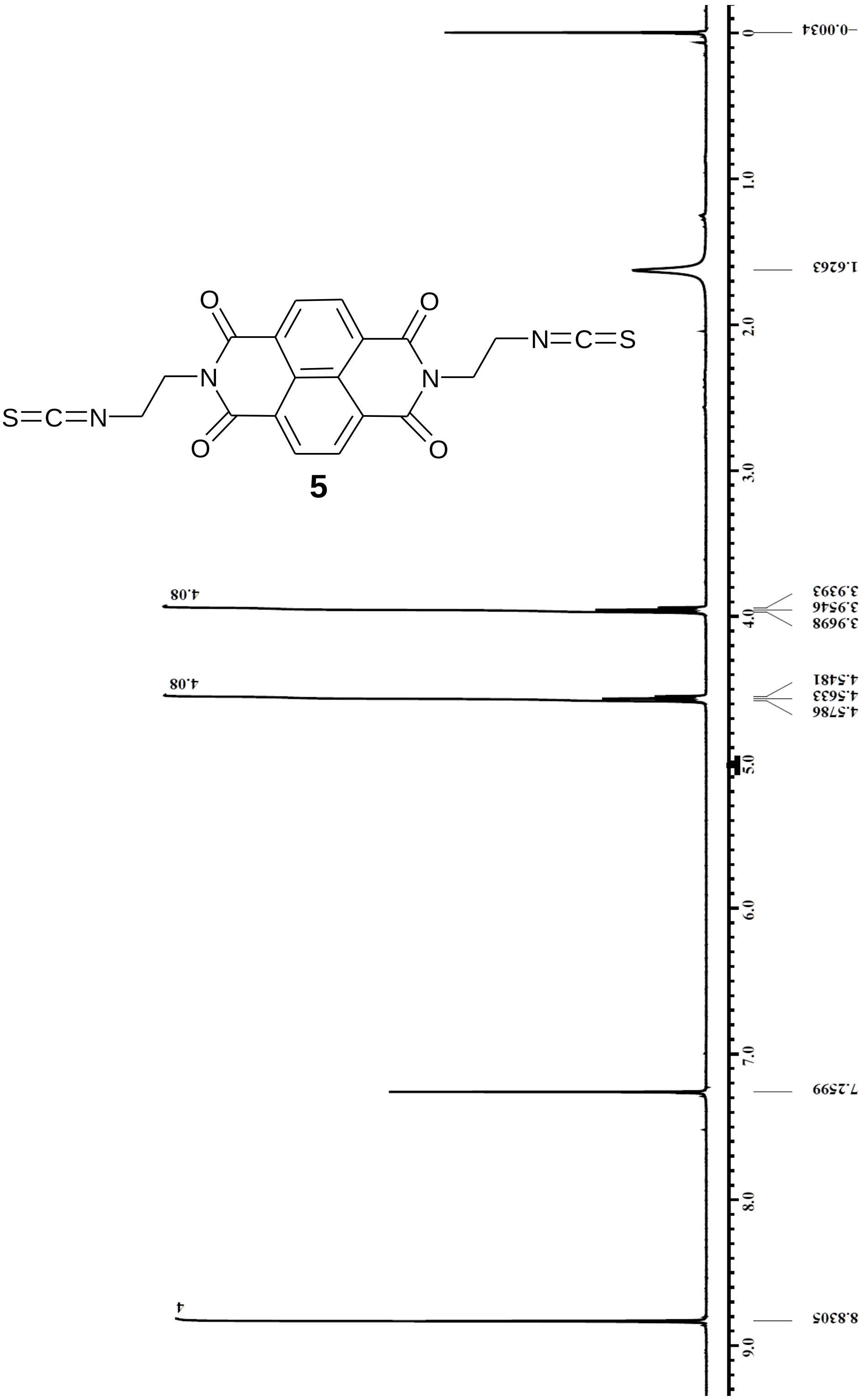

Figure S7. ^{1}H NMR spectrum of isothiocyanate **5**.

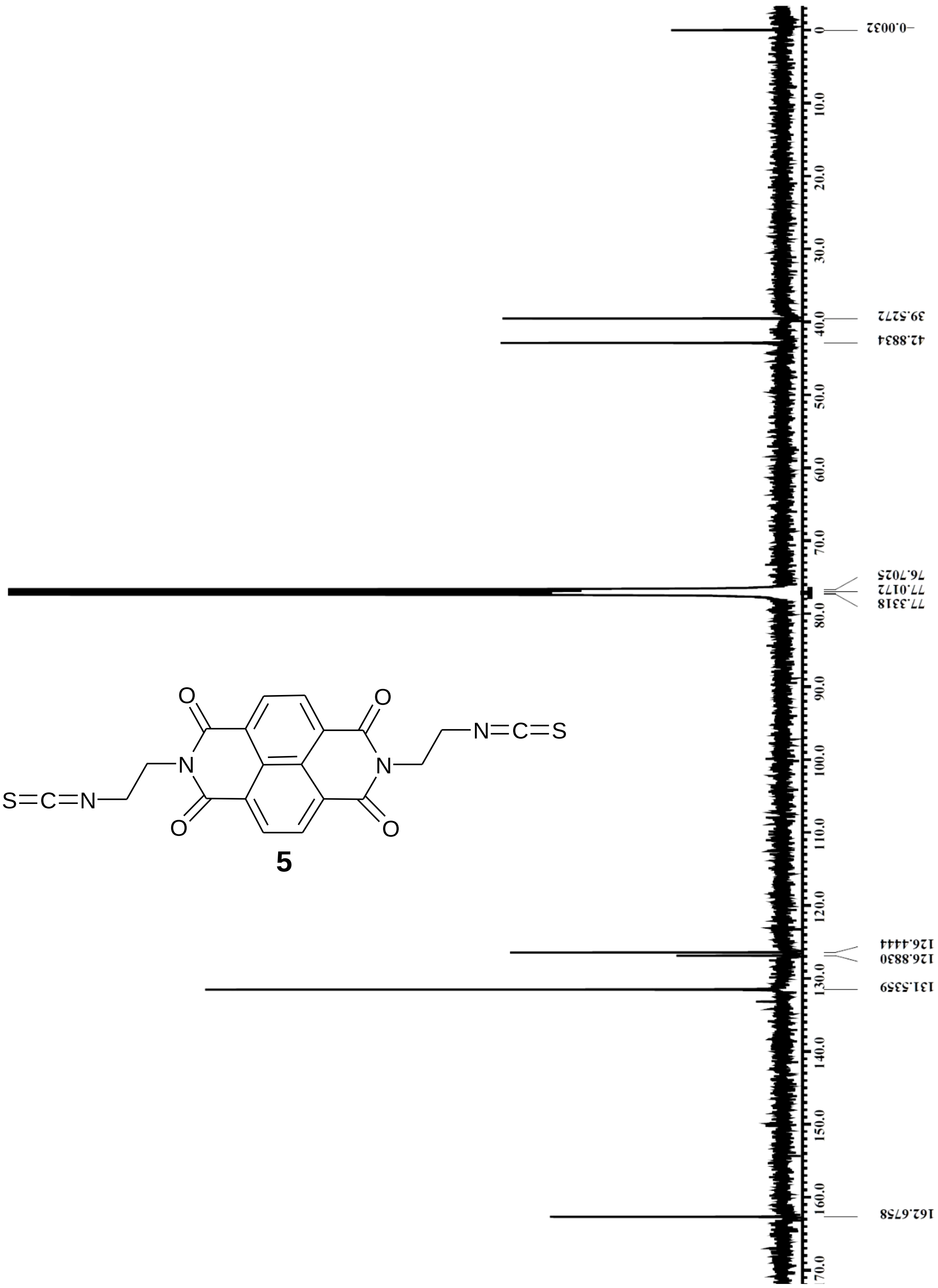

Figure S8. ^{13}C NMR spectrum of isothiocyanate **5**.

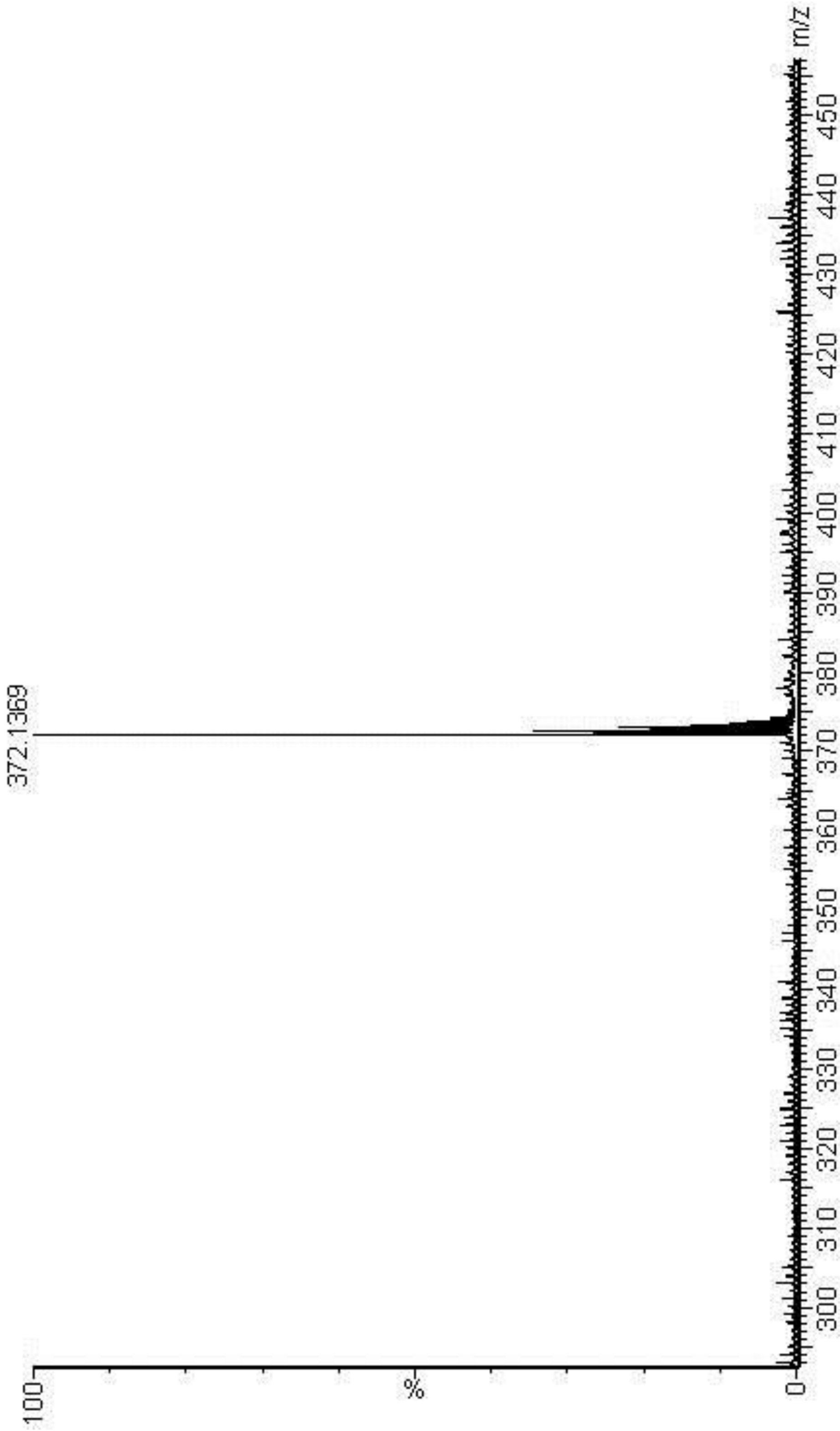

Figure S9. Mass spectrum of the fragment bearing the Hg^{2+} ion contains [**6** + Hg^{2+} + H_2O].

References

1 (a) D. F. Eaton, Luminescence Spectroscopy, in *Handbook of Organic Photochemistry*, ed. J. C. Scaiano, CRC Press, Boca Raton, 1989, **1**, 231; (b) M. L. Sheepwash, R. H. Mitchell, C. Bohne, *J. Am. Chem. Soc.*, 2002, **124**, 4693.