

A Pyridine Dicarboxylate based Hydrazone Schiff Base for Reversible Colorimetric Recognition of Ni²⁺ and PPI

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Experimental

Synthesis of diethyl 2-formyl-6-methyl-4-(4-nitrophenyl) pyridine-3,5-dicarboxylate (**2**)

Selenium dioxide was added to a solution of diethyl 2,6-dimethyl-4-(4-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (**1**) in 1,4-dioxane and the reaction mixture was refluxed for 10 mins to obtain diethyl 2-formyl-6-methyl-4-(4-nitrophenyl)pyridine-3,5-dicarboxylate (**2**) in 59% yield.

The presence of medium peaks at 2860 and 2895 cm^{-1} in the IR spectrum indicated the C-H stretching frequency of $-\text{CHO}$ (aldehyde) group in compound **2**. Further, a sharp band at 1720 cm^{-1} corresponded to the $-\text{C}=\text{O}$ group of aldehyde and the ester groups. The ^1H NMR (Figure 1) displayed characteristic peaks at δ 9.95 (s) which corresponded to the aldehyde proton ($-\text{CHO}$). In the ^{13}C NMR, shown in (Figure 2), the characteristic peak of aldehyde carbon appeared at 192.43 ppm. All the protons and carbons of compound **2** have been assigned in the ^1H and ^{13}C NMR spectra as shown in (Figures 1 and 2). The high resolution mass spectra (HRMS) peak at m/z 387.1187 for $[\text{M}+\text{H}]^+$ ion illustrated the presence of **2** with molecular formula $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_7$.

Synthesis of diethyl (E)-2-((2-(2-hydroxybenzoyl) hydrazono) methyl)-6-methyl-4-(4-nitrophenyl) pyridine-3, 5-dicarboxylate (**DAS**)

The final product **DAS** was synthesized by mixing ethanolic solutions of diethyl 2-formyl-6-methyl-4-(4-nitrophenyl)pyridine-3,5-dicarboxylate (**2**) and 2-hydroxybenzohydrazide (**4**) and adding a few drops of acetic acid to the resulting reaction mixture. This reaction mixture was refluxed for 6 h to obtain **DAS** in 89% yield.

The IR spectrum showed sharp characteristic peaks for $-\text{NH}$ at 2976 cm^{-1} and a broad band for $-\text{OH}$ at 3320 cm^{-1} . In the ^1H NMR (Figure 3), the characteristic peaks of $-\text{NH}$ and $-\text{OH}$ appeared at δ 12.03 ppm and 11.41 ppm, respectively. The imine ($-\text{N}=\text{CH}$) proton occurred at 7.77 ppm. In the ^{13}C NMR, shown in (Figure 4), the characteristic peak of $-\text{N}=\text{CH}$ (imine carbon) appeared at 141.97 ppm. The high resolution mass spectra (HRMS) peak at m/z 521.1621 for $[\text{M}+\text{H}]^+$ ion illustrated the presence of **DAS** with molecular formula $\text{C}_{26}\text{H}_{24}\text{N}_4\text{O}_8$. This spectroscopic data obtained, confirmed the formation of the final product **DAS**.

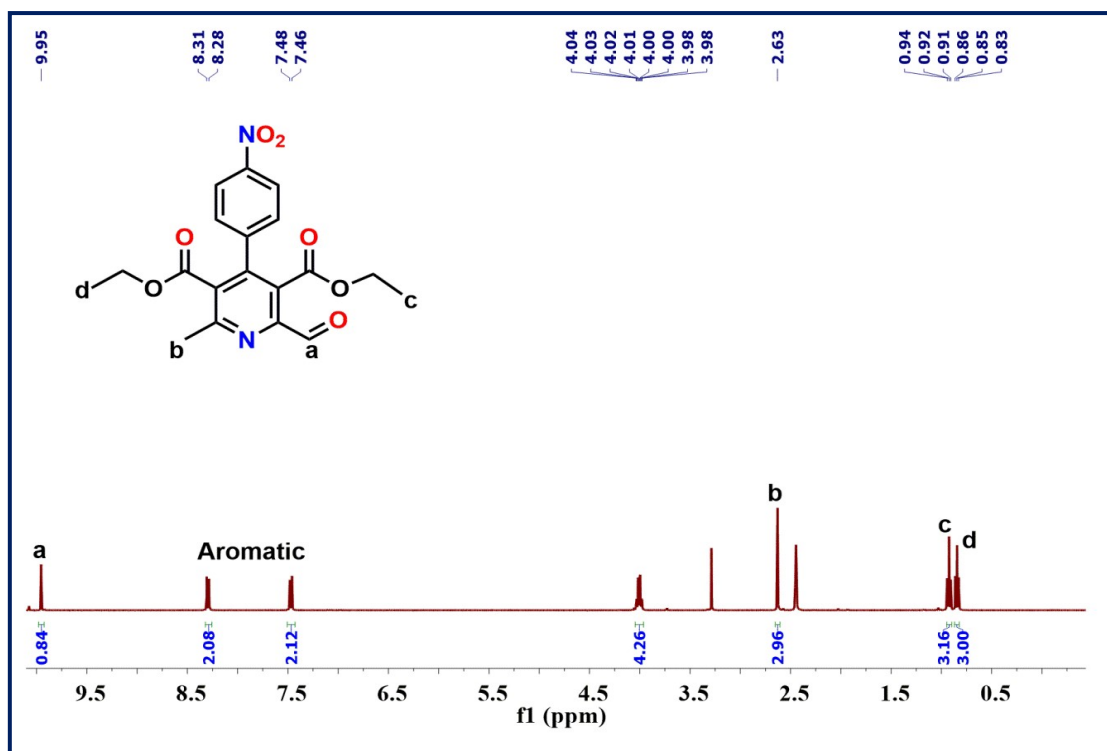


Figure S1: ^1H NMR of compound 2 in $\text{DMSO-}d_6$.

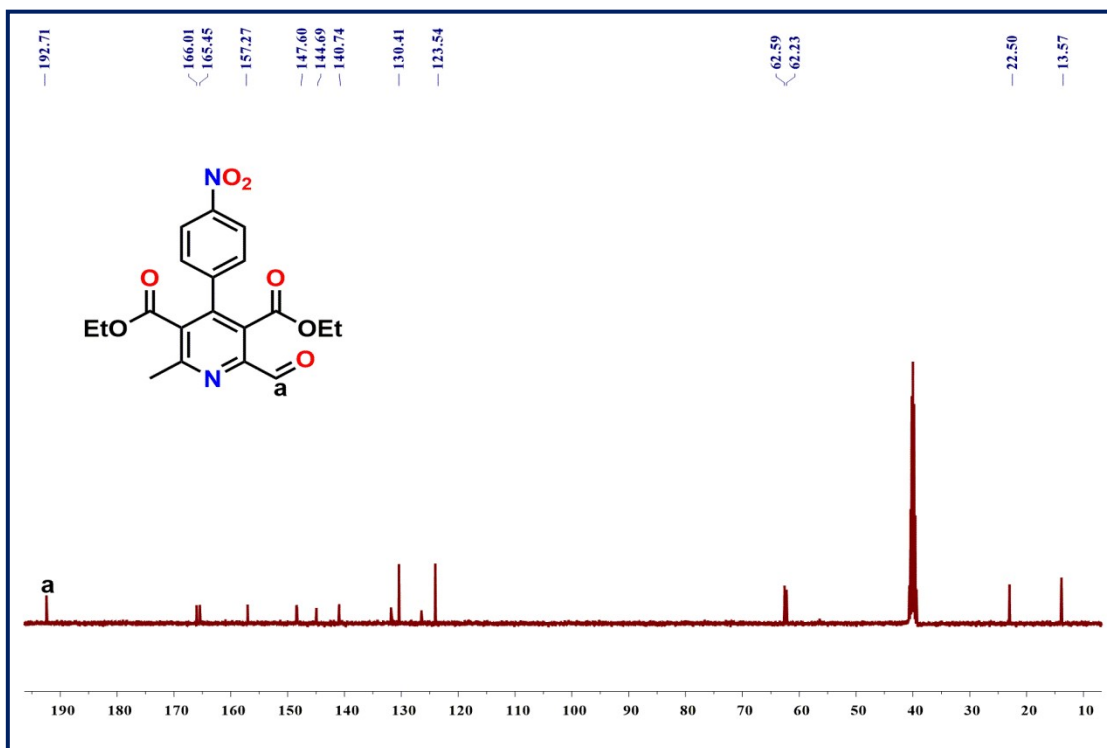


Figure S2: ^{13}C NMR of compound 2 in $\text{DMSO-}d_6$.

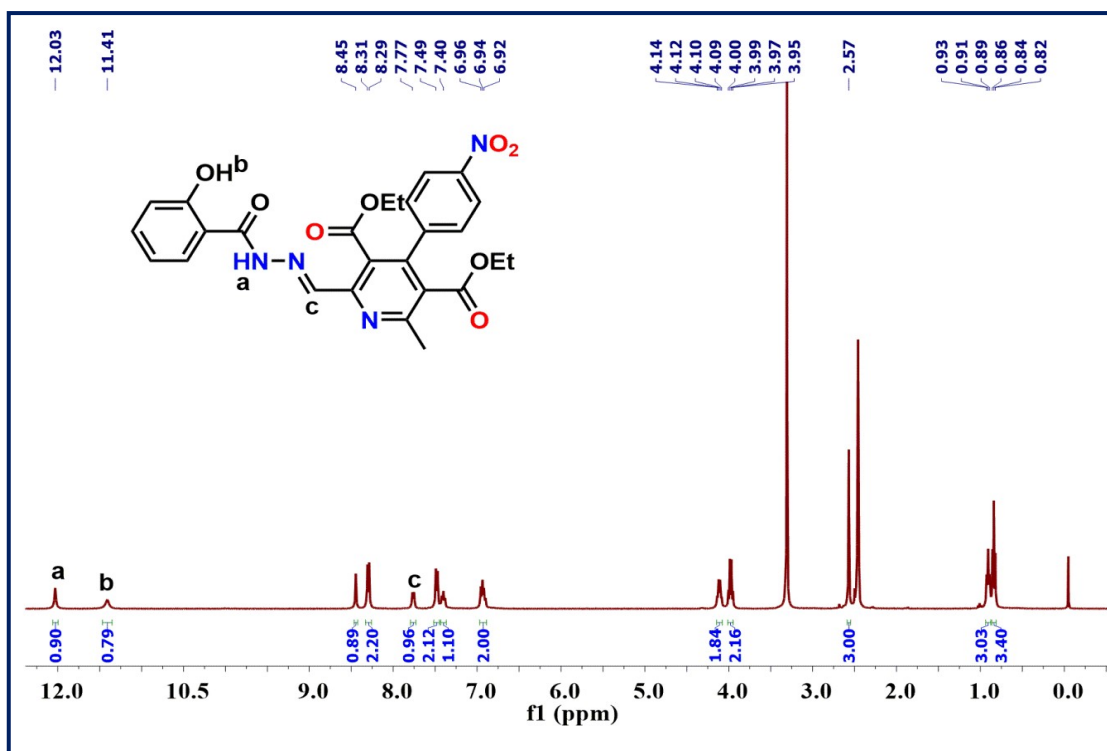


Figure S3: ^1H NMR of DAS in $\text{DMSO-}d_6$

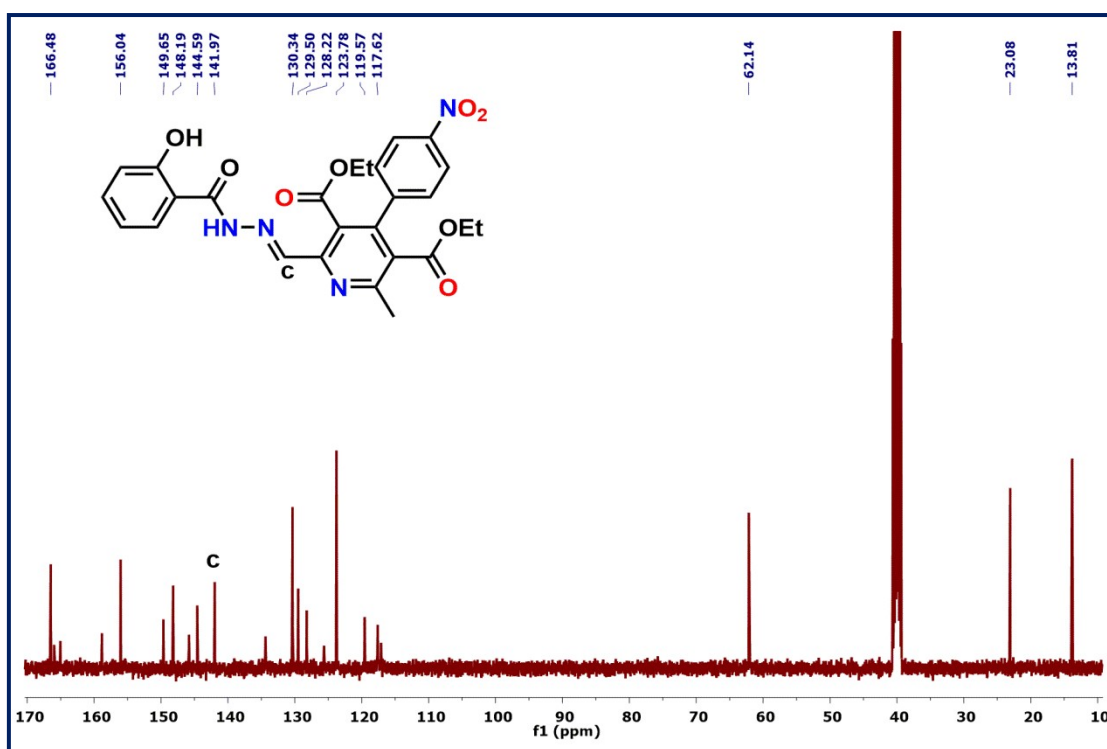


Figure S4: ^{13}C NMR of DAS in $\text{DMSO-}d_6$

Fluorescence spectra

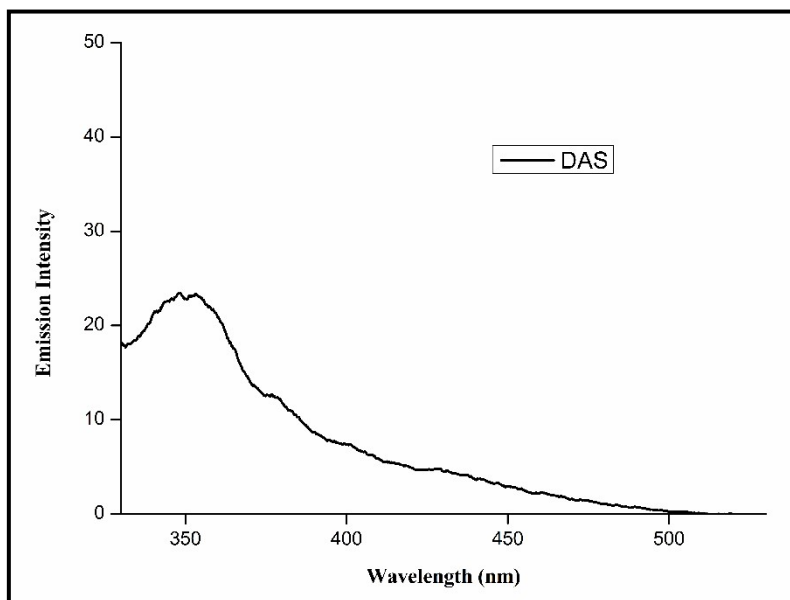


Figure S5: Fluorescence spectra of **DAS**

Single crystal X-ray diffraction analysis

Compound **DAS** was dissolved in methyl alcohol to grow single crystals by allowing slow evaporation of the solvent at room temperature and the metal complex **DAS-Ni²⁺** crystal was obtained by diffusion method layered with acetone for X-ray diffraction studies. The X-ray diffraction data was collected on X'calibur CCD diffractometer employing a graphite monochromatized Mo/K α radiation ($\lambda = 0.71073 \text{ \AA}$) at temperature 100 K for **DAS** and 293K for metal complex. The crystal data was reduced using CrysAlis pro software available with the diffractometer. Further, least square refinement after introduction of anisotropic displacement parameters yielded the R values mentioned in the (**Table 1**) The structure was solved by direct methods using SHELXT-2014 and refined by the full-matrix least-squares method on F^2 (SHELXT-2014/5) . All calculations were carried out using the OLEX2 package of the crystallographic programs. For the molecular graphics, the program Mercury (4.2.0) was used. The selected bond lengths, bond angles, *etc.* are given in (**Table 1**).

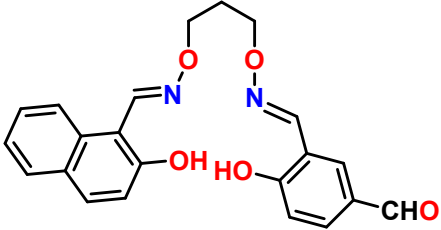
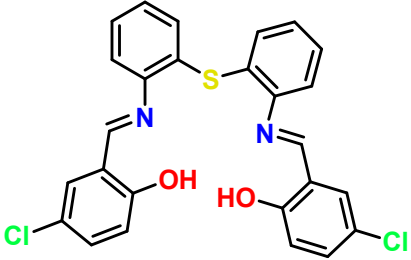
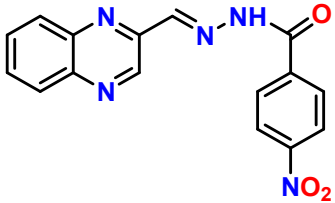
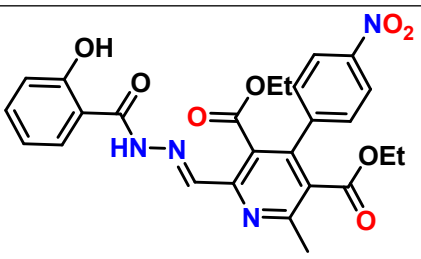
Table S1 Crystal data and structure refinement for compound **DAS** and metal complex

Identification code	DAS	DAS-Ni ²⁺
Empirical formula	C ₂₆ H ₂₄ N ₄ O ₈	C ₂₀₈ H ₁₆₉ N ₃₂ O ₆₆ Ni ₄
Temperature/K	100	296(2)
Crystal system	monoclinic	monoclinic
Space group	P 21/n	P-1
a/Å	7.2016 (3)	16.418(6)
b/Å	18.2857 (12)	19.301(7)
c/Å	18.8379 (13)	35.287(12)
α/°	90	82.233(8)
β/°	97.855 (3)	90
γ/°	90	90
Volume/Å ³	2457.4 (3)	11080(7)
Z	49	139
ρ _{calc} /cm ³	1.4068	2.119
μ/mm ⁻¹	0.106	5.814
F(000)	1088.6424	6950.0
Radiation	Mo/K _α (λ = 0.71073)	Mo/K _α (λ = 0.71073)
2θ range for data collection/°	2.230 to 28.04	1.919 to 27.824
Index ranges	-10 ≤ h ≤ 10, -10 ≤ k ≤ 10, -20 ≤ l ≤ 20	-21 ≤ h ≤ 21, -25 ≤ k ≤ 25, -45 ≤ l ≤ 45
No of Reflections measured	10693	51315
Independent reflections	5644	11466
Goodness-of-fit on F ²	1.0076	1.168
R [F ² > 2σ (F ²)], wR(all data)	0.0981, 0.1436	0.2187, 0.3936

Accession Codes

CCDC 2206485 and 2206486 contain the supplementary crystallographic data for ligand as well as metal complex for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033

Table S2 Sensing abilities of various chemosensors for Ni²⁺ ions and phosphate reported in literature

S.No.	Chemosensors	Ions Detected	Phosphate Detection	Detection Limit (in μM)	Ref.
1.		Ni ²⁺	HPO ₄ ²⁻	0.03	1
2.		Ni ²⁺	-	0.361	2
3.		Ni ²⁺	-	1.47	3
4.		Ni ²⁺	PPi	0.14	Present Work

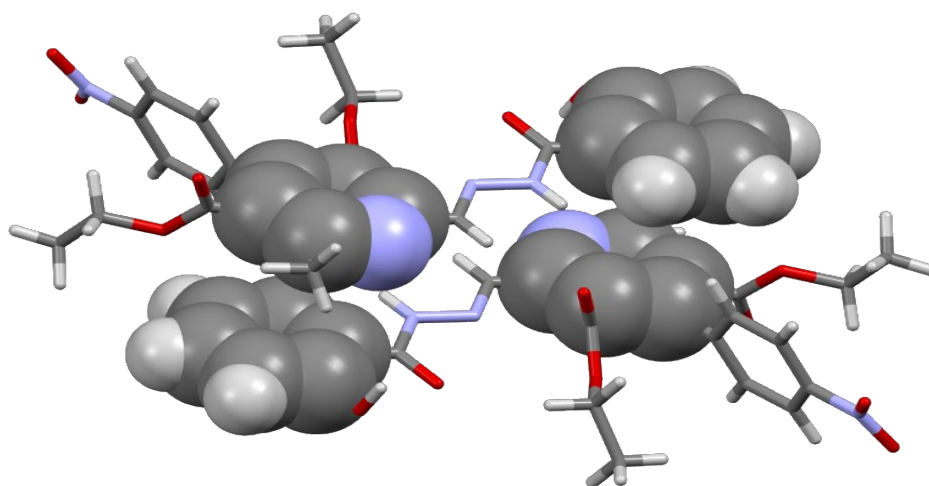


Figure S6: Double decker π -stacked arrangement of two Phenolic and Pyridine ring between the adjacent molecules.

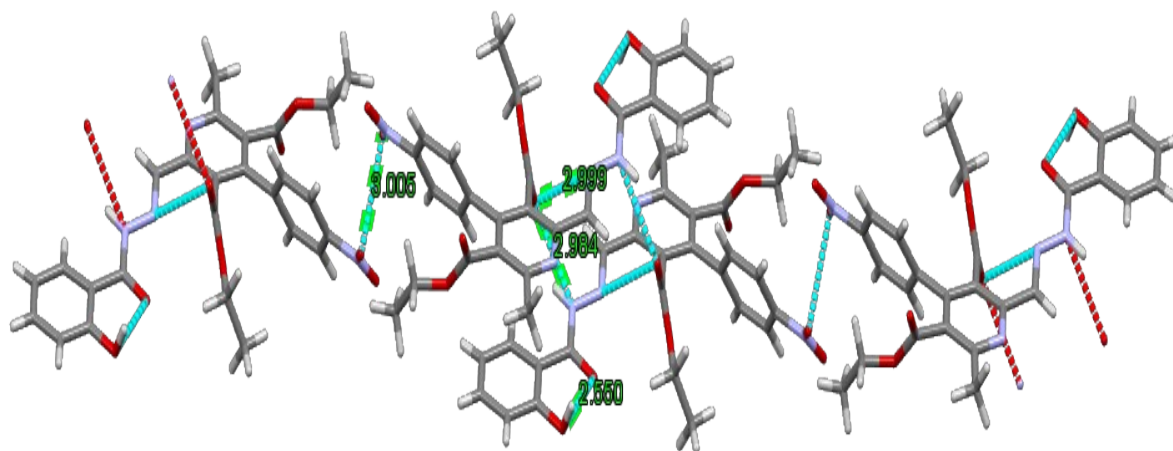


Figure S7: 1D arrangement of DAS *via* intra- and intermolecular non-covalent interactions between the adjacent molecules.

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