Supporting Information

Analysis of the contribution of the π-acidity of the *s*-tetrazine ring in the crystal packing of coordination polymers

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Figure S1. Views of a set of parallel 2D sheets (shown in black, red, green and blue) that give inclined interpenetration with the reference orange framework.

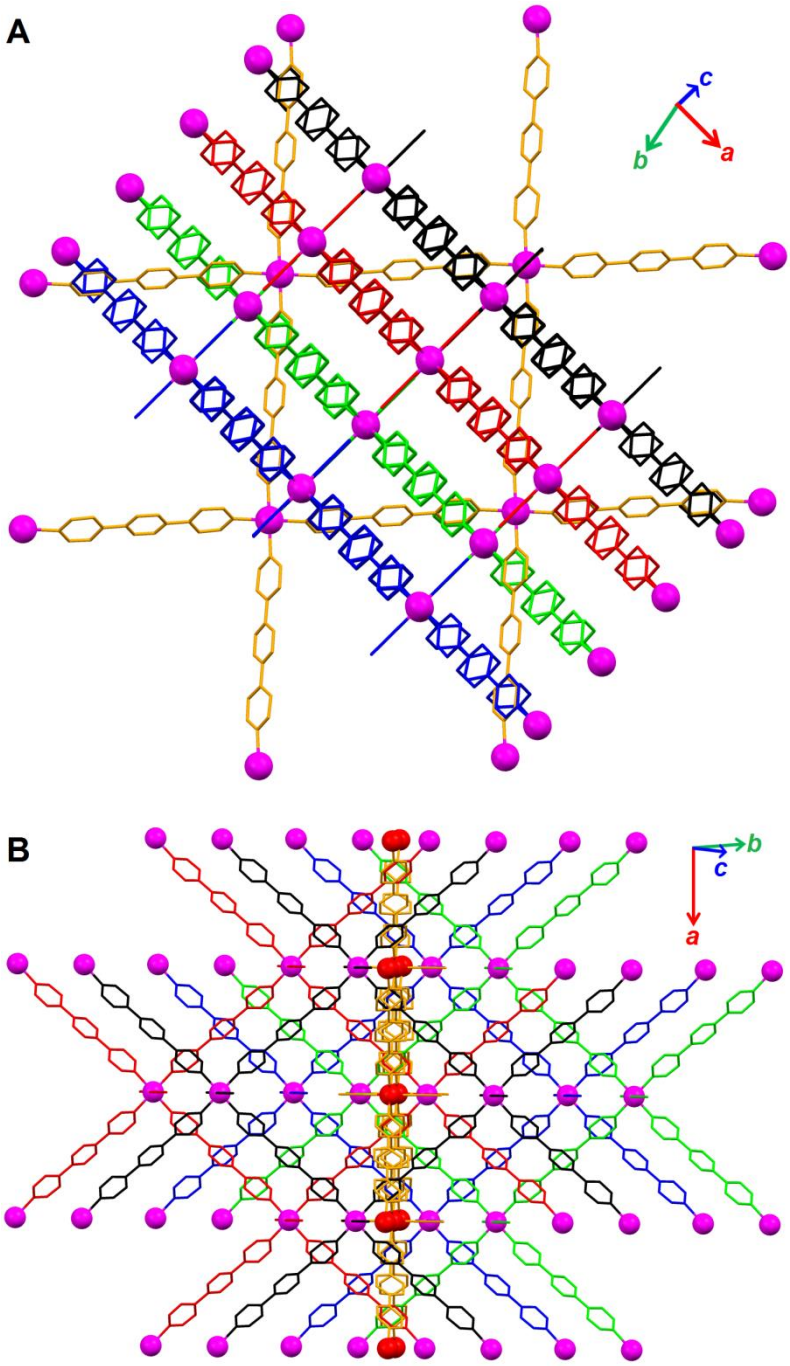

Figure S2. Supramolecular interactions stabilizing the solid-state structure of 1; A) π•••π interactions between pyridine (centroid Cg1) and tetrazine (centroid Cg2) rings (Cg1•••Cg2 = 3.881(2) A; B) lone pair•••π contacts between thiocyanate sulfur atoms (S1) and pyridine (Cg1) rings (Cg1•••S1 = 3.730(2) A).

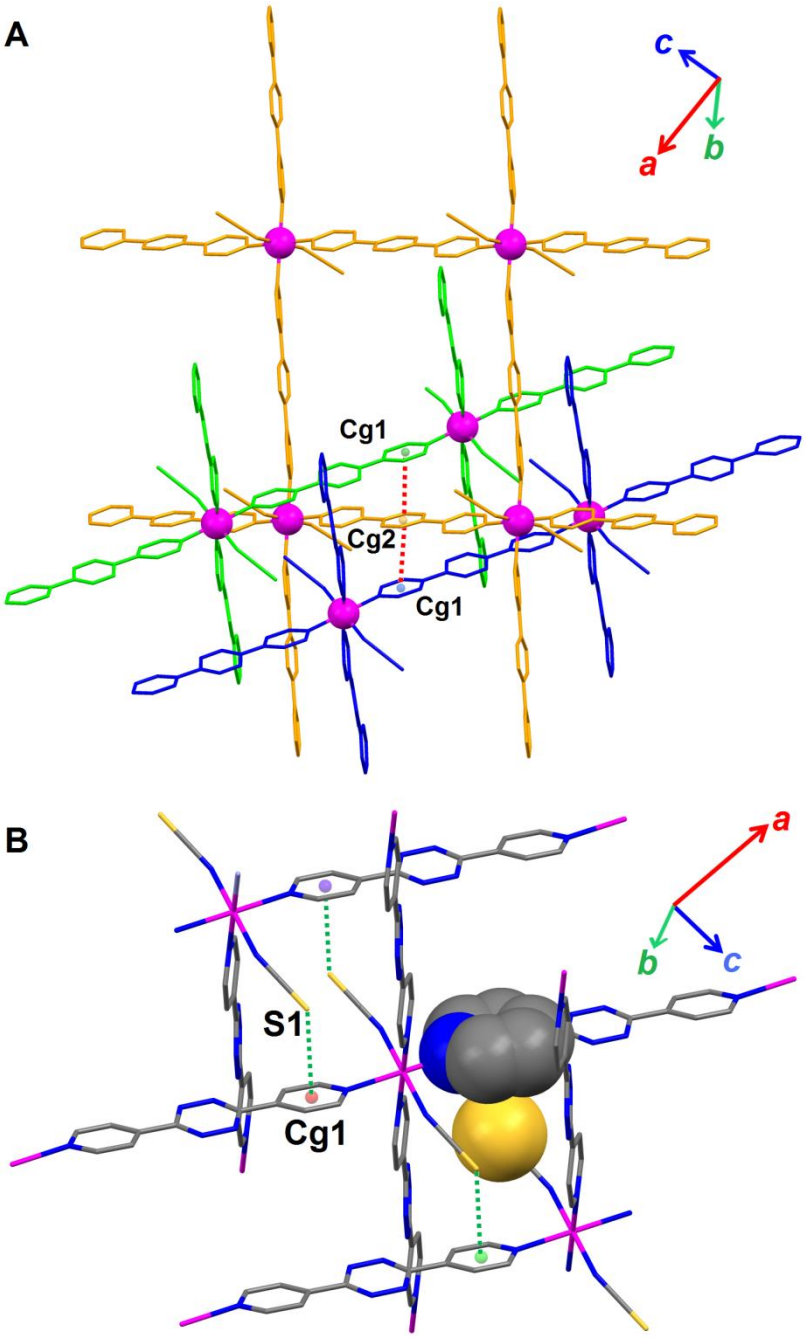

Figure S3.A) Hydrogen bonds along the crystallographic b axis connecting the 1D chains; B) formation of a supramolecular 2D sheet in the *ab* plane.O3–H41•••O1 = 2.772(3) Å and ∠ O3–H41–O1 = 167(3)°.

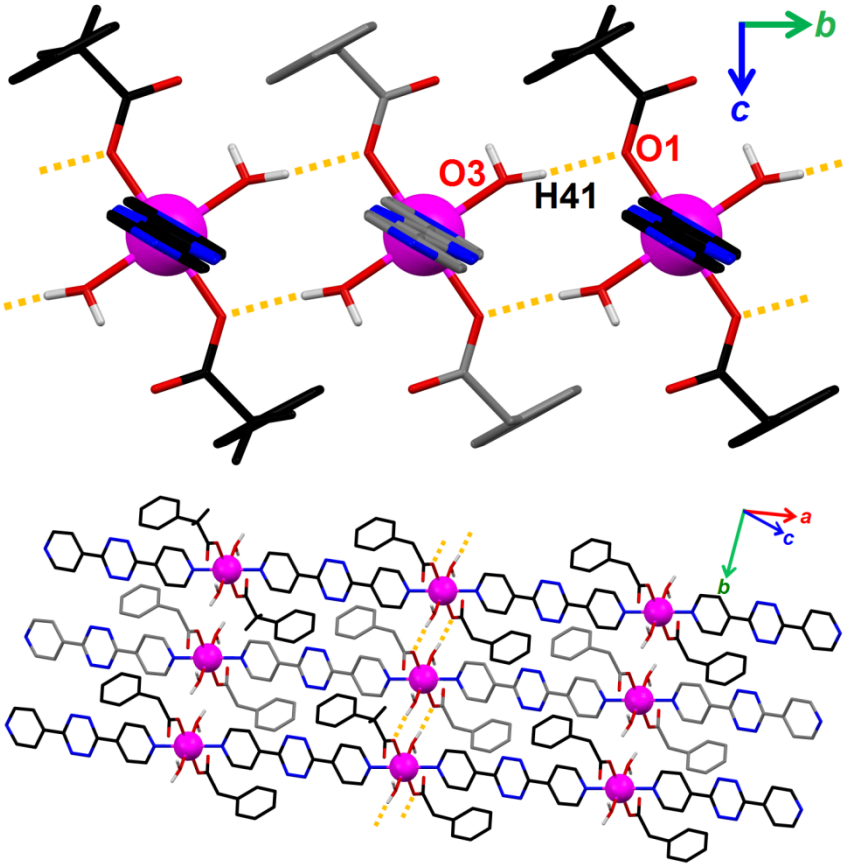

Figure S4.A) Illustration of the crystal packing of **2** showing the formation of a 3D framework through $\pi_{Phe}\cdots\pi_{tz}$ interactions, with centroid-to-centroid distances Cg2···Cg3 of 3.581(3) Å. The inset picture indicates the two short bonding contacts, i.e. C1···C9 = 3.366(4) Å and N3···C11 = 3.249(4) Å, characterizing this parallel-displaced π–π stack. Three 2D hydrogen-bonded sheets are depicted in different colours.

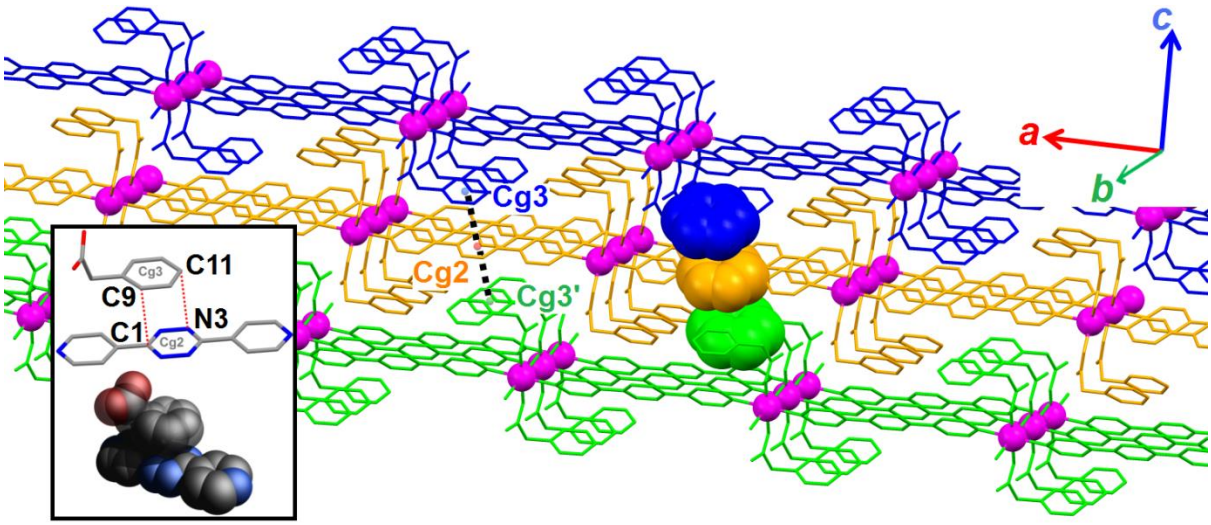

Figure S5. Illustrations of the layer-by-layer 3D assembly of 2D rhombohedral grids by means of π···π interactions (centroid-to-centroid Cg9···Cg13 distance of 3.669(5) Å). Three rhombohedral-grid layers are represented with different colours. The inset picture indicates the short bonding contact, *i.e.* C66···C16 = 3.377(12) Å.

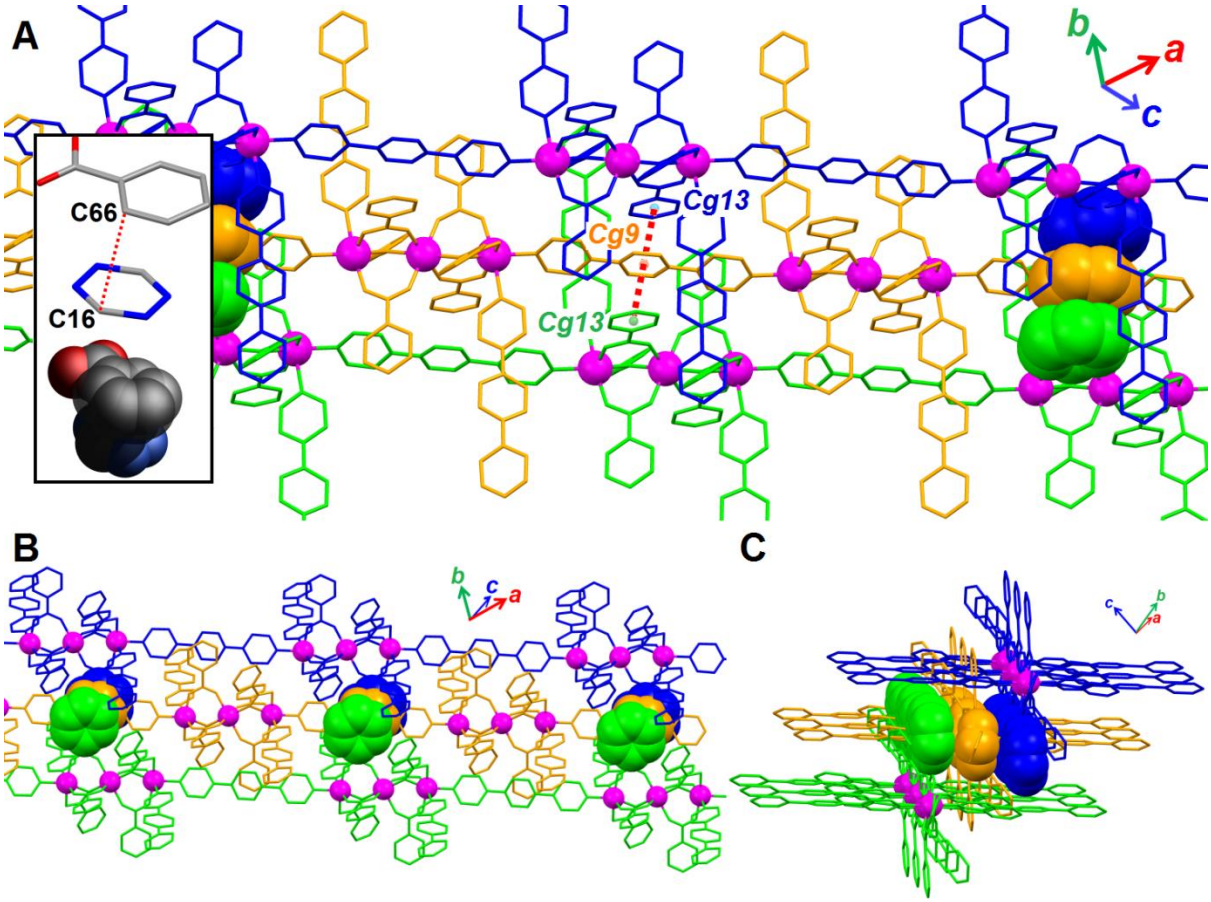

Figure S6. IR spectrum of the free ligand pbptz.

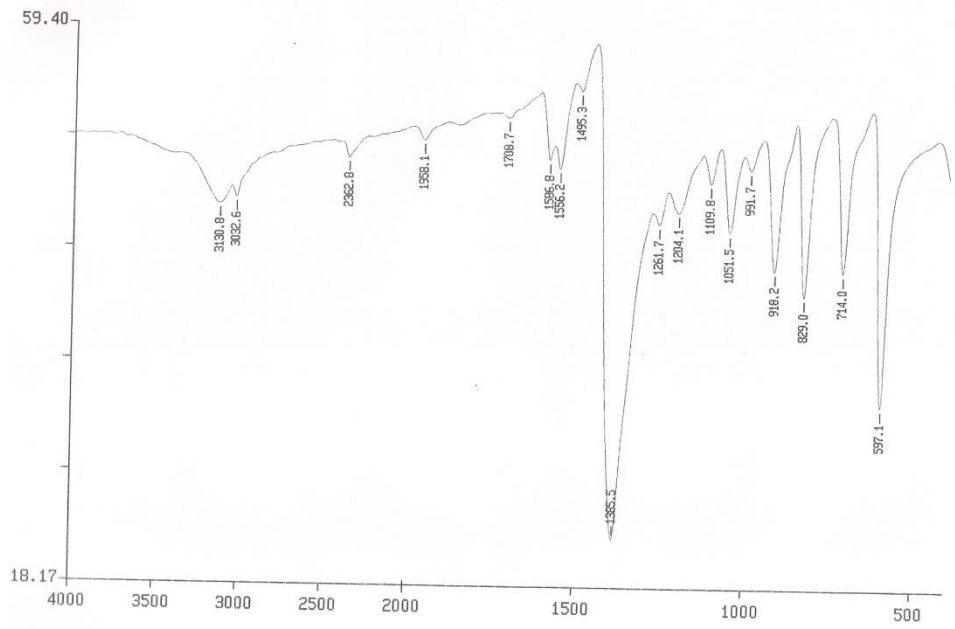

Figure S7. IR spectrum of complex **1**.

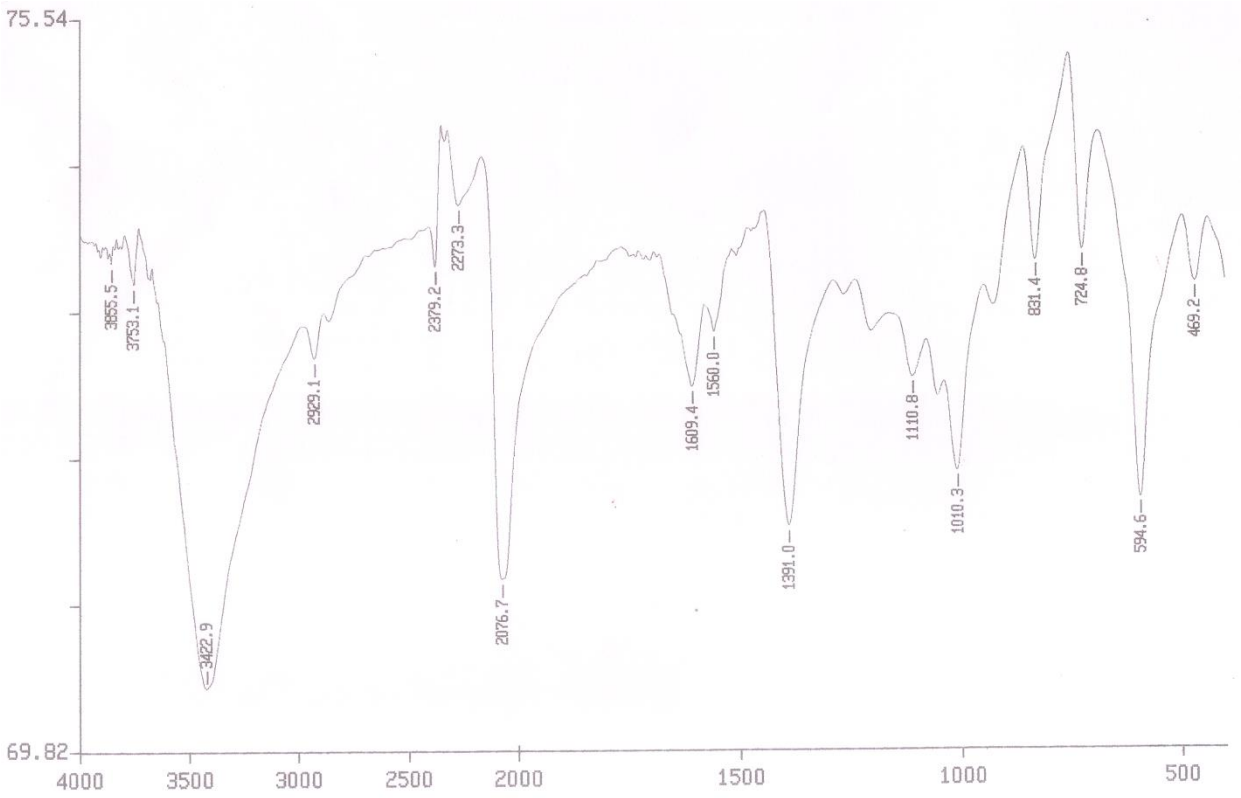

Figure S8. IR spectrum of complex **2**.

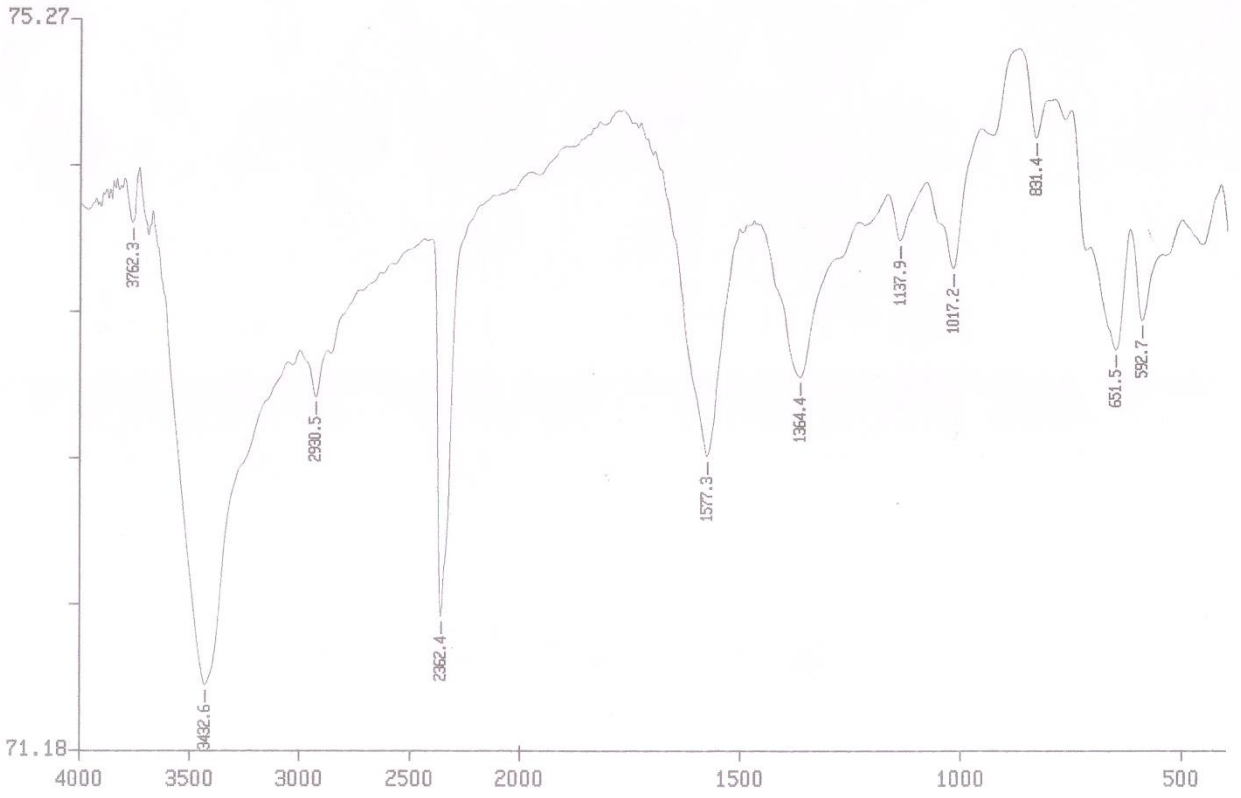

Figure S9. IR spectrum of complex **3**.