Supplementary Information

In-situ synthesis of 5-substituted-tetrazoles and their metallosupramolecular coordination polymers

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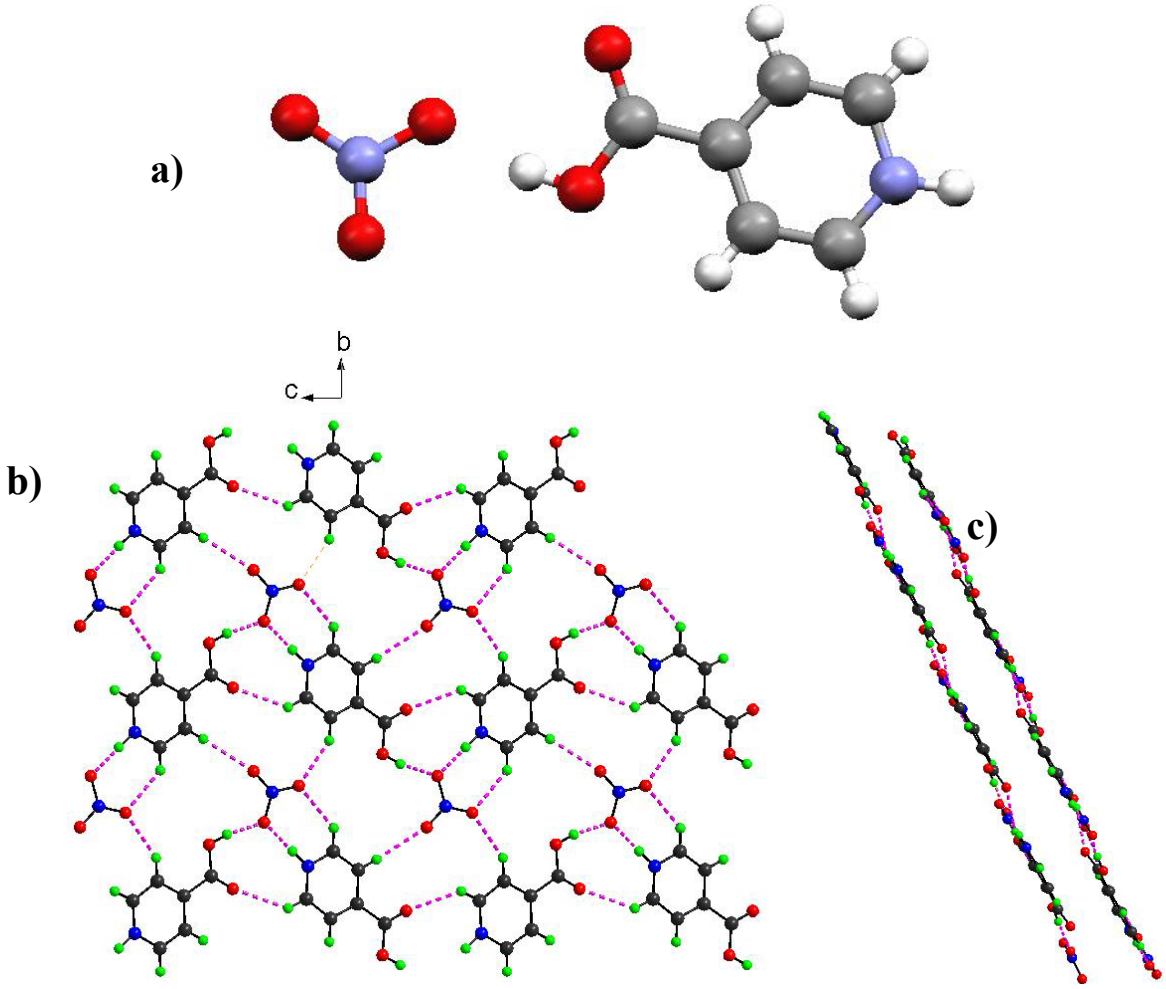

Figure S1: a) Structure of $[HOOC\text{-}pyH]^+(NO_3^-)$. b) Each nitrate anion connects to four $[HOOC\text{-}pyH]^+$ cations via O-H···O, N-H···O and C-H···O hydrogen bonds to form a supramolecular sheet. c) π-π Stacking between neighbouring supramolecular sheets.

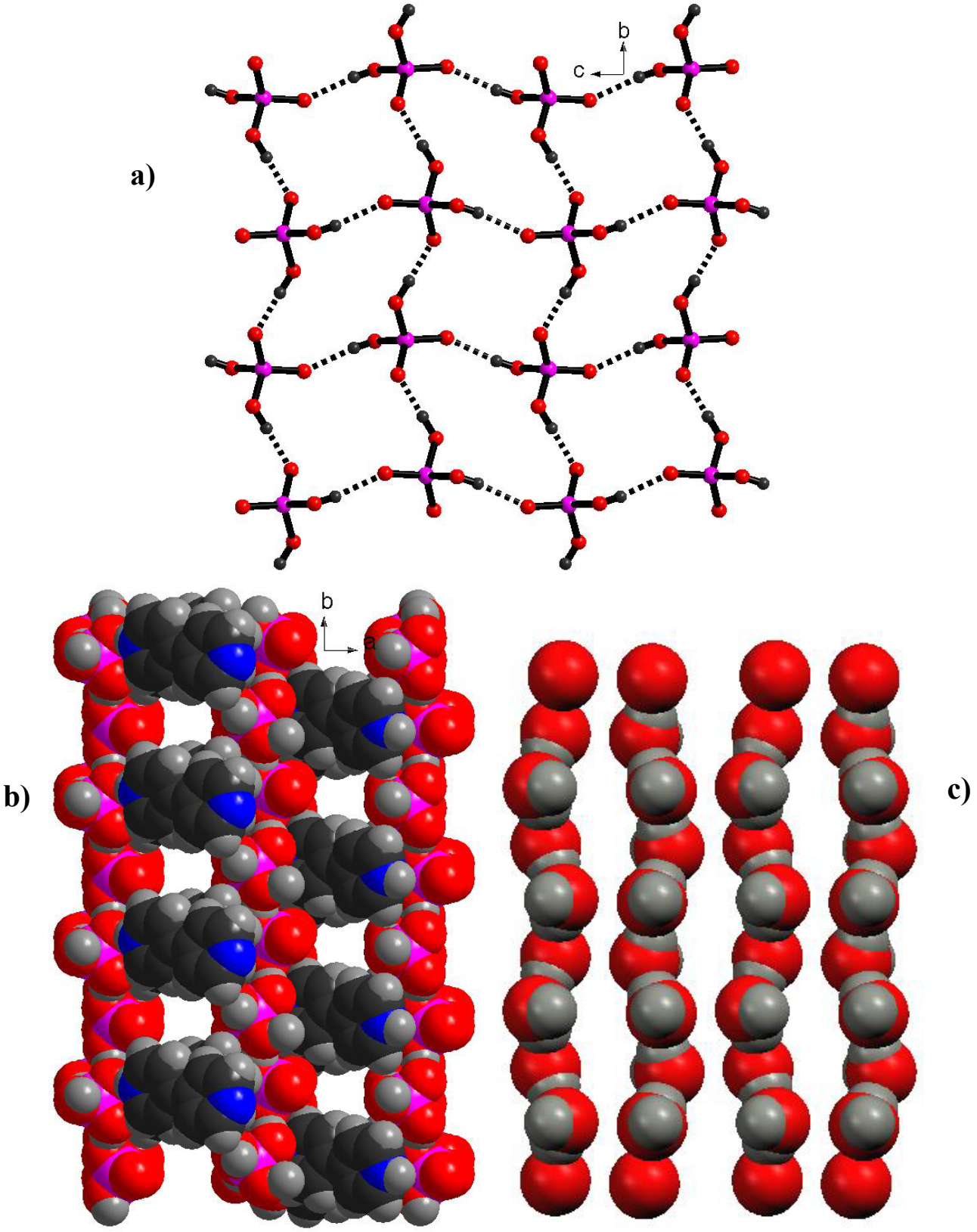

Figure S2: Structure of $[(4,4'\text{-bipyH}_2)(H_2PO_4)(H_2O)_2]$. a) $H_2PO_4^-$ anions are hydrogen-bonded to form anionic sheets. b) $4,4'\text{-bipyH}_2^{2+}$ cations act as pillars connecting $\{H_2PO_4^-\}_n$ via N-H···O hydrogen-bonding into a pillared supramolecular network with channels. c) left- and right-handed water chains located in the channels shown in b).

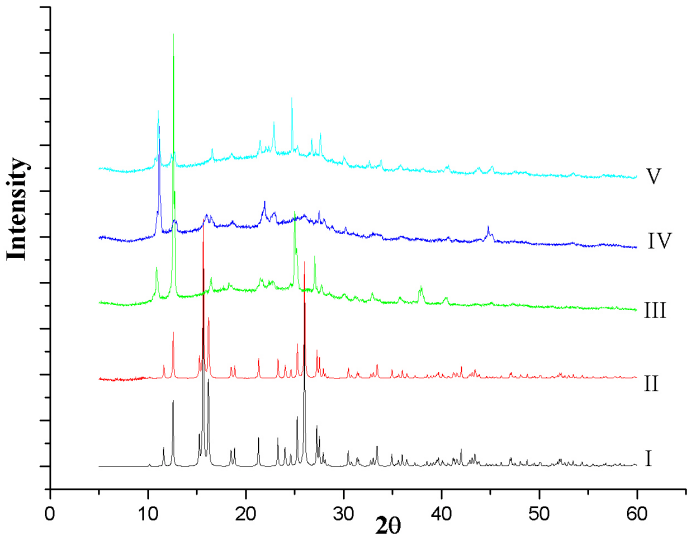

Figure S3: PXRD data for $[Zn(pytz)_2(H_2O)_4]\cdot 2H_2O$ (**3**). (I) Simulated from single-crystal diffraction data; (II) as-synthesized **3**; (III) crystalline phase **3a** obtained by heating of **3** at 170°C for 3 hours under N_2 flow (60 ml min^{-1}); (IV) sample of **3b** obtained after **3a** was exposed to air for one day; (V) sample of **3c** obtained by heating **3b** at 170°C for one day under N_2 flow (60 ml min^{-1}).

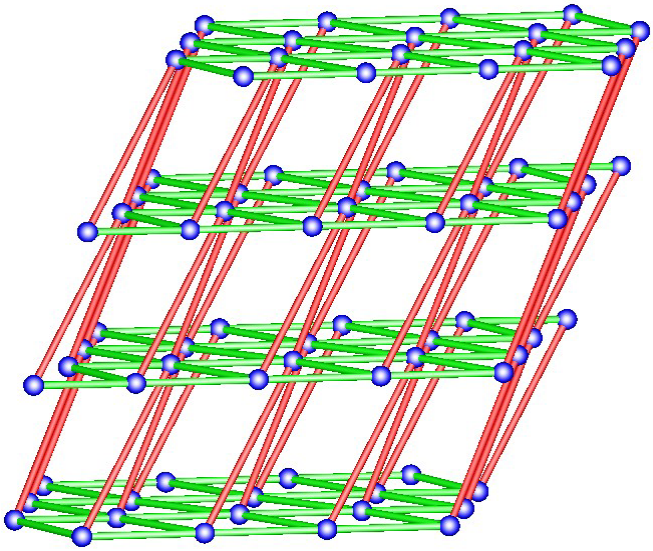

Fig. S4: Three-dimensional 6-connected contorted α-Po net in **2** with $4^{12}\cdot 6^3$ topology (viewed close to [010] direction).

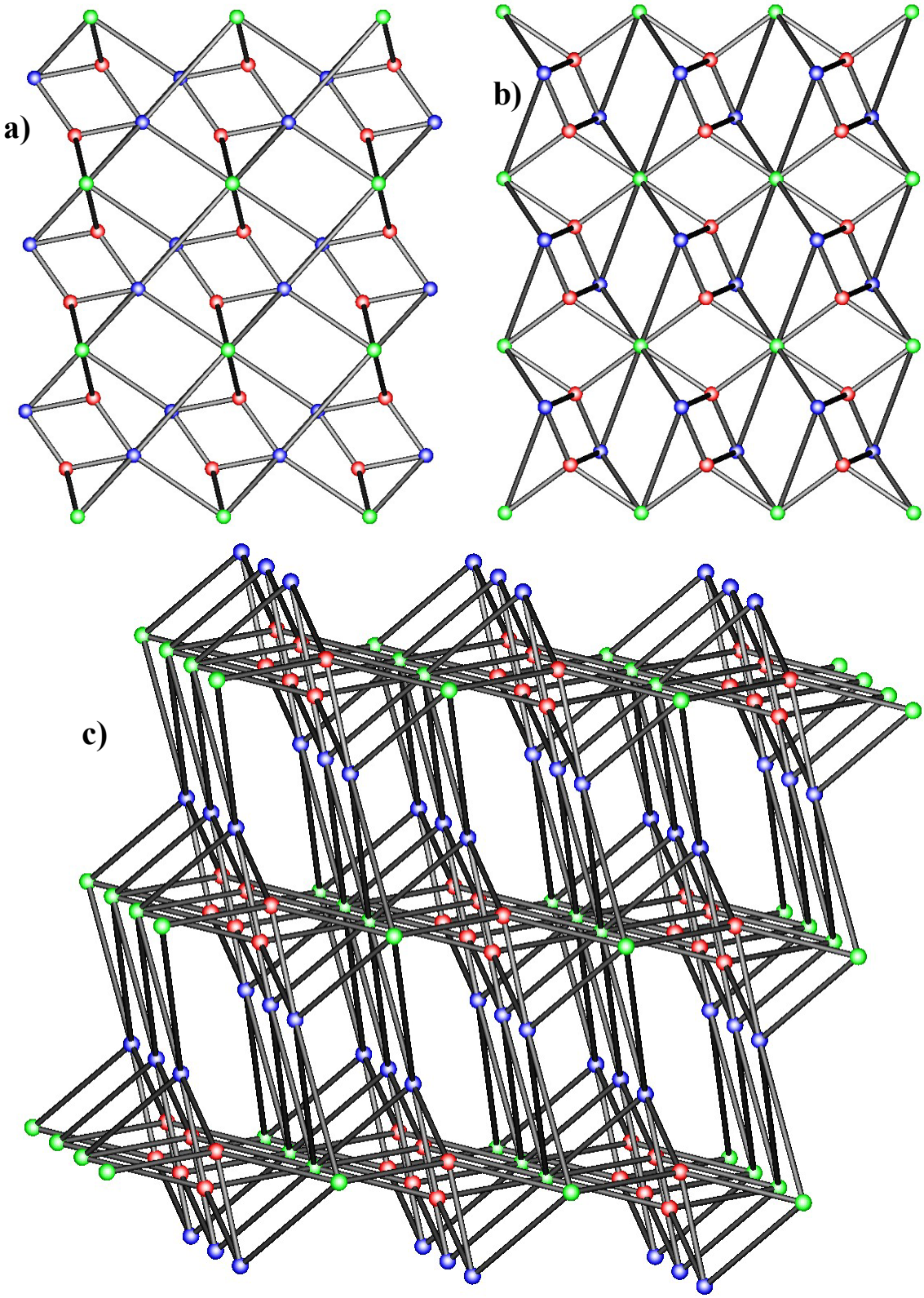

Fig. S5: 3D (4,5,10)-connected trinary net with $(3{\cdot}4^2{\cdot}5^3)_2(3{\cdot}4^4{\cdot}5^4{\cdot}6)_4(3^2{\cdot}4^8{\cdot}5^{14}.6^{12}{\cdot}7^7{\cdot}8^2)$ topology for **3**. a) viewed along a axis, b) viewed along b axis, c) viewed close to [001] direction.

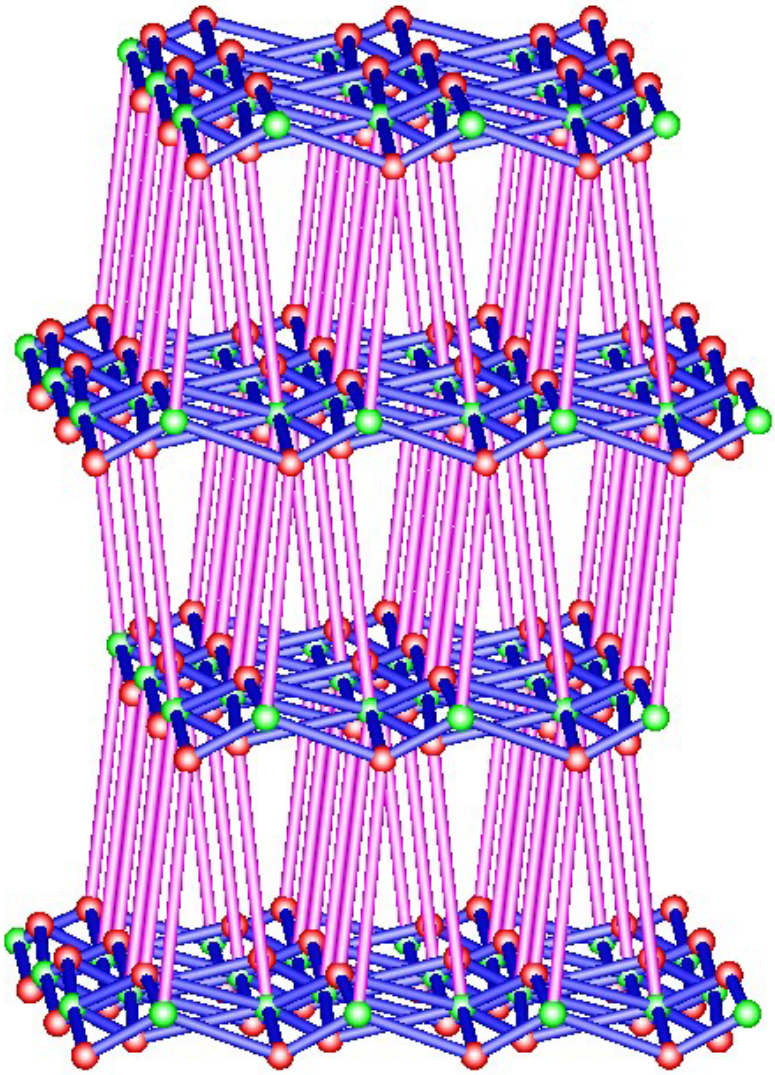

Fig. S6: 3D (4,8)-connected binary $(4^6)_2(4^{12}\cdot6^{12}\cdot8^4)$ net for **4** (viewed close to [001] direction), comprising of (3,6)-connected layers and linear pillars.

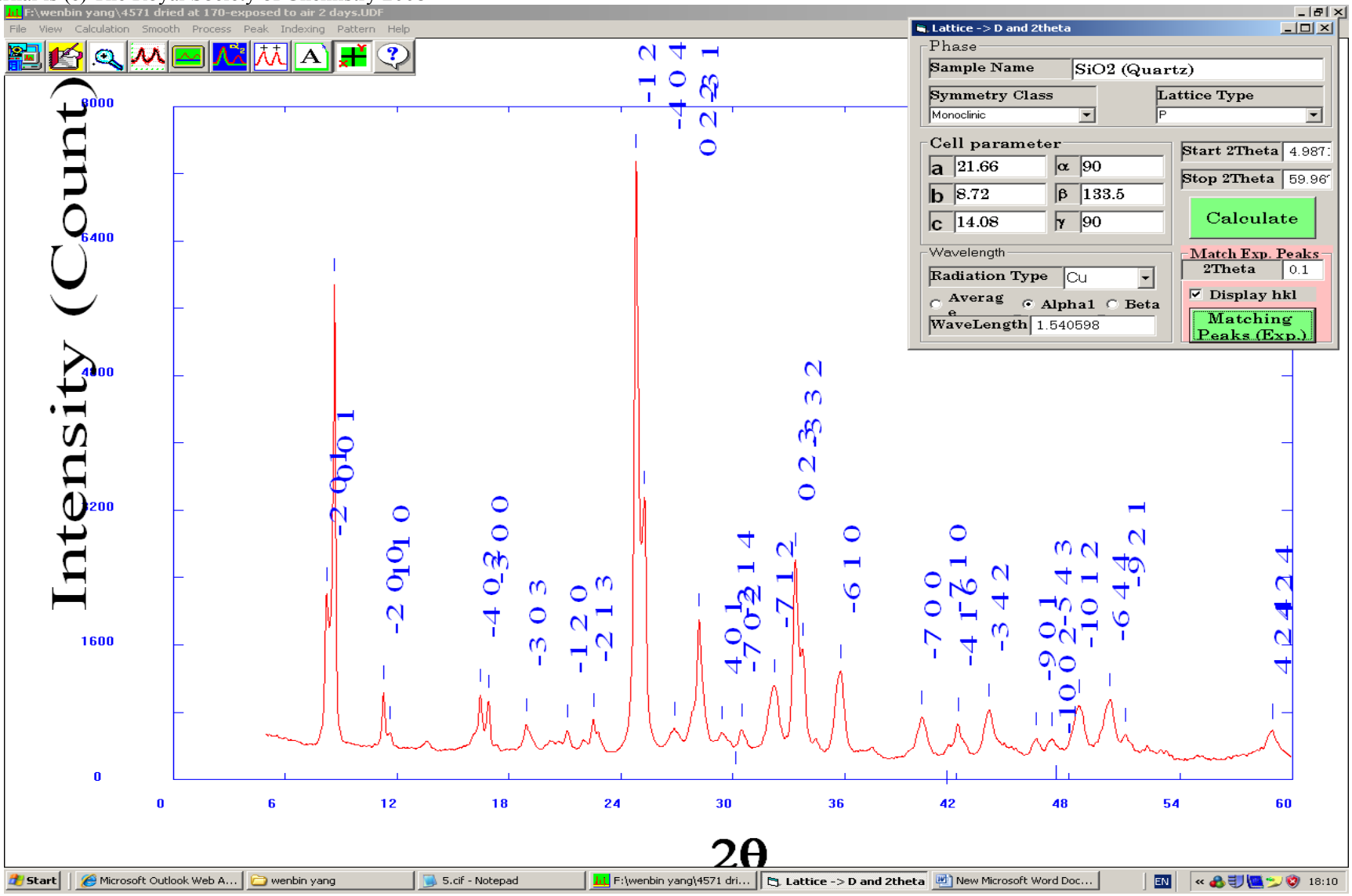

Fig. S7 The indexing of PXRD patterns of **4c** giving a monoclinic *P* unit cell with $a = 21.66$, $b = 8.72$, $c = 14.08$ Å and $\beta = 133.6$