Supplementary information: Investigating the electronic properties of novel Titanium Oxonitridophosphate, $Ti_5P_{12}N_{24}O_2$, through structural distortions at the Titanium sites

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I. CRYSTAL FIELD PARAMETER ($10D_q$, Ds, Dt)

Fig. S1 shows the experimental Resonant Inelastic X-ray Scattering (RIXS) spectrum of the titanium oxonitridophosphate compound $Ti_5P_{12}N_{24}O_2$. The initial energy values for crystal field parameters, namely $10Dq$, Ds, and Dt, were achieved through analysis of the experimental RIXS spectrum of $Ti_5P_{12}N_{24}O_2$. Notably, the Δ_{t2g} was identified to be at 0 eV, attributed to a convolution in the elastic peak, while the energy splitting for the eg orbitals, Δ_{eg}, was found to be 1.4 eV. The energy difference between the elastic peak and the first inelastic feature, representing 10Dq, was determined to be 0.4 eV.

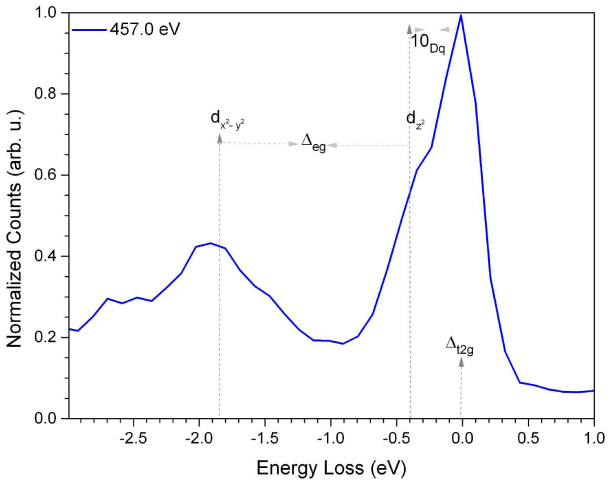

FIG. S1: *Figure S1 is the measured RIXS spectrum showing the distortion parameter 10Dq and the energy gap Δ_{eg} and Δ_{t2g} orbitals of $Ti_5P_{12}N_{24}O_2$.*

$$d_{x^2-y^2} = 6 \times 10Dq + 2 \times Ds - Dt, \tag{S1}$$

$$d_{z^2} = 6 \times 10Dq - 2 \times Ds - 6 \times Dt, \tag{S2}$$

S1 - S2 = S3

$$\Delta_{eg} = 4 \times Ds + 5 \times Dt, \tag{S3}$$

$$d_{xy} = -4 \times 10Dq + 2 \times Ds - Dt, \tag{S4}$$

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$$d_{xz,yz} = -4 \times 10Dq - Ds + 4 \times Dt. \tag{S5}$$

S4 - S5 = S6

$$\Delta_{t2g} = 3 \times Ds - 5 \times Dt, \tag{S6}$$

$$Ds = 0.20 \tag{S7}$$

$$Dt = 0.12 \tag{S8}$$

Utilizing these parameters and solving the equations S3 and S6 simultaneously, we obtain the values of Ds and Dt to be 0.20 eV and 0.12 eV, respectively.

II. DETERMINING SPLITTING ENERGIES: CALCULATION METHODOLOGIES

The following parameters V_{b1g}, V_{a1g}, V_{b2g} and V_{eg} are used to represent the 3d-orbital energy level for D_{4h} symmetry. The Hamiltonian[1–3] for the system is set up in the Lua script for Quanty[4–7], incorporating terms for the crystal field, spin-orbit coupling, electron-electron interactions, and hybridization parameters.
A Python script performs parameter fitting by adjusting the hybridization parameters (among others) to fit the calculated and measured spectra. This process involves multiple steps such as running Quanty simulations with initial guesses for the parameters, comparing the simulated XAS and RIXS spectra to experimental spectra, and using optimization Powell fitting algorithm[8] to adjust all the variable parameters iteratively, minimizing the difference between theoretical and experimental spectra. This process involves analyzing the spectral features such as peak positions, intensities, and shapes to ensure that the model accurately reflects experimental observations.
The fitting process is inherently iterative, requiring multiple simulations with Quanty, each time adjusting the parameters based on the outcome of the previous fit. The ultimate goal is to minimize the discrepancy between the calculated and experimental spectra within acceptable limits.
Upon optimizing the fitting parameters, we calculate the corresponding splitting energy of the e_g orbitals Δ_{eg} and t_{2g} orbitals Δ_{t2g} as shown in equation S3 and equation S6 respectively.

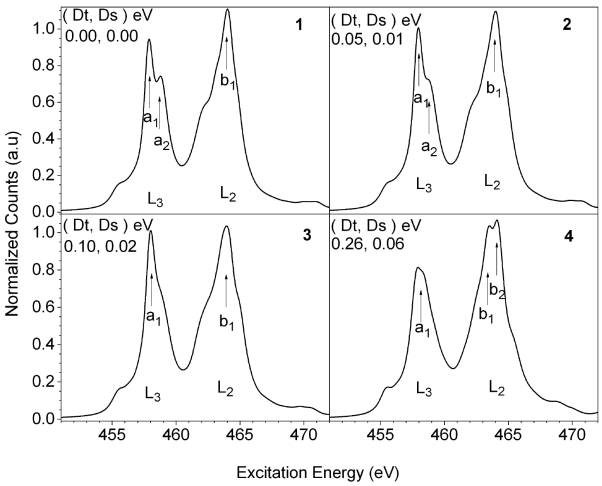

FIG. S2: *Figure S2 (1-4) shows the impact of the increasing distortion parameters Ds and Dt on $Ti_5P_{12}N_{24}O_2$ XAS spectra. "a_n" and "b_n" represent features on the L_3 and L_2 -edge. Increasing the energy values Ds and Dt, the enhanced L_3 (a_2) feature in (1) becomes broaden and reduced in intensity, whereas in (4) a new feature (b_2) emerges in the L_2-edge.*

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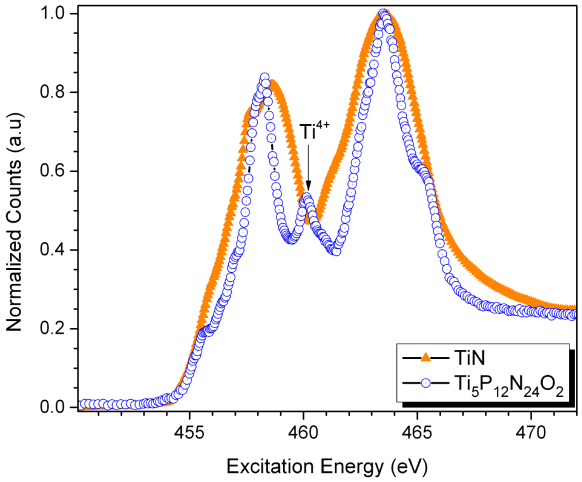

FIG. S3: *Figure S3 shows an overlay of $Ti_5P_{12}N_{24}O_2$ (blue circle) and TiN (orange triangle) XAS spectra.*

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