Supporting Information

An organic-inorganic hybrid material constructed from three-dimensional coordination complex cationic framework and entrapped hexadecavanadate clusters

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Single crystal X-ray diffraction study:

A dark specimen of **1** (0.25×0.24×0.18 mm) having a octahedral morphology was picked up with paraton oil on the tip of a glass capillary tube and mounted on a Rigaku RAXIS RAPID IP diffractometer equipped with a graphite-monochromated Mo-K_α (λ = 0.71073 Å) radiation source. The data were corrected for Lorentz and polarization effects , and empirical absorption corrections based on equivalent reflections were applied. A successful structure solution was obtained in the non-centrosymmetric space group P-4n2 (No. 118) with the Flack parameter 0.59. Just like the program (SHELXTL[1]) suggested, the crystal may be racemic twinning. We carried out X-ray diffraction study on another single crystal. However, a similar result was obtained. In the structure, guest 4,4'-bpy molecules are severely disordered and can't be well modelled. A best model adopted is represented in Fig. S4. When checking the structure with PLATON, the relative bigger shift values have been alerted with suggested additional refinement cycles. Those problems are likely resulted by the poor model of disordered 4,4'-bpy guests. So the SQUEEZE routine of the PLATON software[2] was applied to create a new reflection data where contributions from the disordered guests are removed from the original data. The refinements of the guest-free structure on the squeezed data converged to R1 = 0.0550 and wR2 = 0.1382. (CCDC 276945) When the guest-free structure was check by PLATON again, all those mentioned alerts have gone. However, there are alerts about the existence of additional (pseudo) symmetry elements all the time. We attempted to get a successful structure solution in the higher symmetrical space group *P*4(2)/nnm (No. 134) however failed. It is possible that not all the atoms have the higher symmetry.

References

[1] G. M. Sheldrick, SHELXTL-PLUS. *Crystal Structure Analysis Package*; Bruker Analytical X-ray, Madison, WI, 1997.

[2] Platon program: A. L. Spek, *Acta Crystallogr. Sect. A*, 1990, **46**, 194-201.

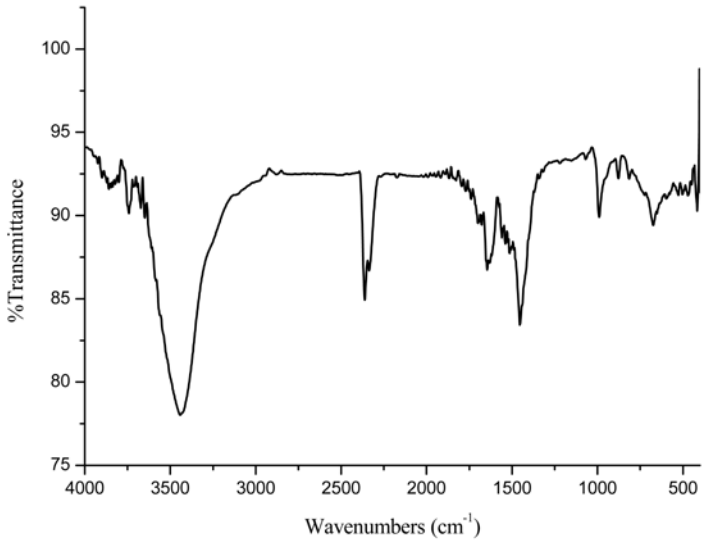

Fig. S1. FT-IR spectra of as-synthesized samples.

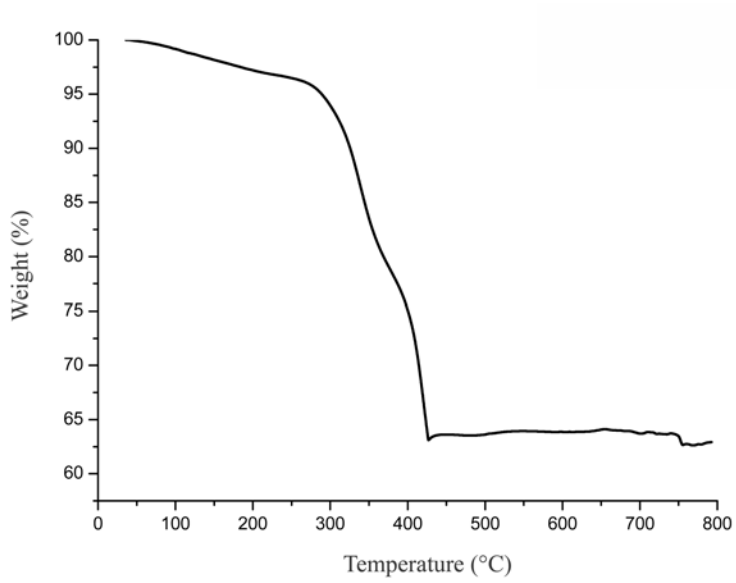

Fig. S2. TG curve of as-synthesized **1**. Heating rate: 10 deg sec^{-1}, N_2 atmosphere. A continuous weight loss (36.7%) until 426 °C corresponds to the removal of six guest water molecules, one guest 4,4'-bpy molecule and four coordinated 4,4'-bpy molecules (calcd.36.1%).

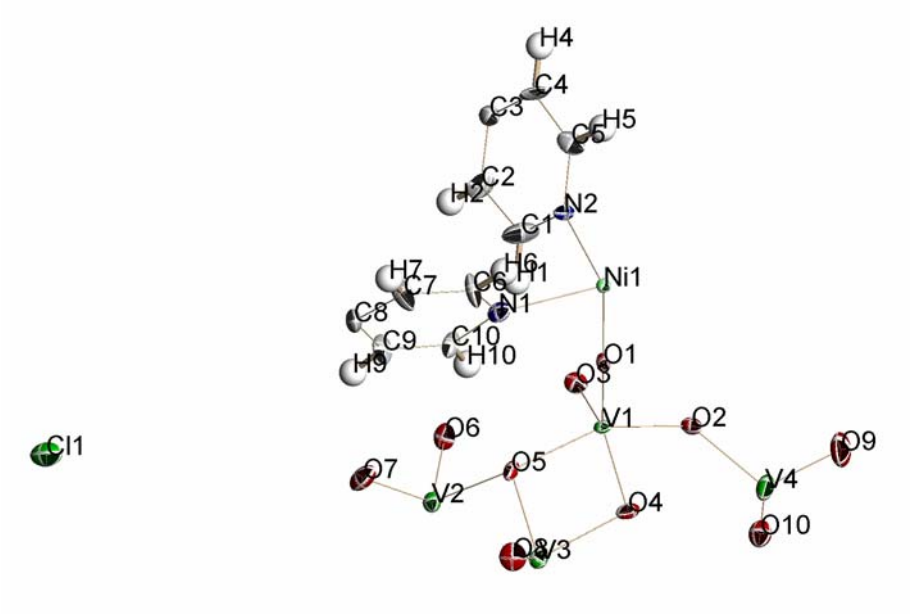

Fig. S3. Asymmetric unit of 1 with all the nonhydrogen atoms represented by 30% thermal ellipsolids. Disordered guests are not shown for clarity.

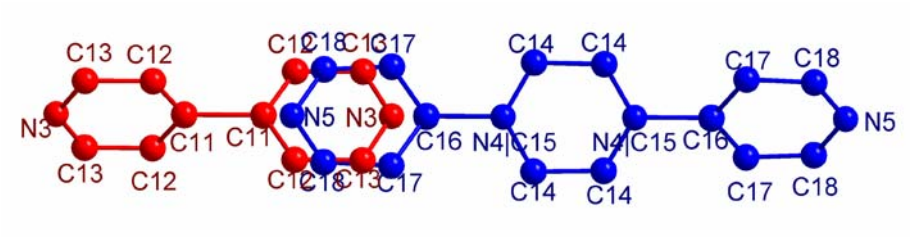

Fig. S4. The 4,4'-bpy guests are disordered in three positions: one is represented in red; (occupation: 50%) the other two are represented in blue.(occupation: 25%) N4 and C15 on the same position.