Supporting information

Layered V-B-O Polyoxometalate Nets Linked by Diethylenetriamine Complexes with Dangling Amine Groups

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1. Synthesis

1.1 Synthesis of SUT-12

SUT-12 was synthesized from the boric acid reflux method. All the chemicals were used as received from the company without further purification. 0.5 mmol of NH_4VO_3 and 2 mmol $NH_4B_5O_8.4H_2O$, 20 mmol H_3BO_3, 0.5 mmol $Zn(NO_3)_2.6H_2O$ were mixed together in a 23 ml Teflon tube, and 0.2 ml distilled H_2O and 0.44 ml $NH(CH_2CH_2NH_2)_2$ were added subsequently. The telflon tube was put into the stainless steel autoclave, heated in 180 ºC for 7 days, and then cooled down to room temperature. The extra H_3BO_3 was washed away by 80 ºC hot water. Colourless block crystals with a typical size around 40 micrometers together with some tiny aggregated crystals with a typical size around 10 micrometer named as VB-7 were obtained. Unlike the boric reflux method employed in synthesis of pure aluminoborates such as PKU-1 and PKU-2, which can be obtained as a pure phase quite easily, it was difficult to obtain a pure SUT-12 although a lot of experiments were performed.

1.2 Synthesis of SUT-13

SUT-13 was synthesized from hydrothermal method. All the chemicals were used as received from the company without further purification. 0.5 mmol of V_2O_3 and 2 mmol $NH_4B_5O_8.4H_2O$, 2 mmol H_3PO_4, 1 mmol $Cu(NO_3)_2.3H_2O$ were mixed together in a 23 ml Teflon tube, and 9 ml distil H_2O and 0.22 ml $NH(CH_2CH_2NH_2)_2$ were added subsequently. The Teflon tube was put into the stainless steel autoclave, heated in 120 ºC for 12 days, and then cooled down to room temperature. Prism dark blue SUT-13 crystals with shining copper metal crystals were harvested after washed by distilled water.

2. Characterization

2.1 Single Crystal X-ray diffraction

Single crystal X-ray diffraction data for SUT-12 and SUT-13 were collected at room temperature on an Oxford Diffraction Xcalibur 3 diffractometer, with Mo Kα radiation (λ = 0.71073 Å). The single crystal X-ray diffraction data for VB-7 was collected in Diamond synchrotron light source at the beam line I19 due to the small crystal size around 10 micro meter. Data reduction was performed using the CrysAlisPro program[1]. Gaussian absorption correction was applied to SUT-12 and SUT-13, and multi-scan absorption correction was applied to VB-7. All structures were solved by direct methods. Non-hydrogen atoms were located directly from difference Fourier maps. Final structure refinements were performed with the SHELX program[2,3] by minimizing the sum of the squared deviation of F^2 using a full matrix technique. Due to the small crystal size, we tried our best to get a reasonable data for this phase in I19, but due to the relative big unit cell and low symmetry, the data still lacking of completeness as required by IUCr, but the present data should be enough for confirming the cluster type in VB-7 phase. The final crystallographic data and refinement details were listed in Table S1.

Table S1. Crystal data and refinement details of structure determination of SUT-12, SUT-13 and VB-7 from single crystal X-ray diffraction.

Identification code	**SUT-12**	**SUT-13**	**VB-7**
Temperature/K	298	298	100
Wavelength/Å	0.71073	0.71073	0.6998
Crystal system	Triclinic	Trigonal	Monoclinic
Space group	*P*-1	*R*-3	*C2/c*
Unit cell dimensions	a=11.8651 Å, b=13.2312 Å, c=13.2880 Å, α=61.735°, β=79.118°, γ=65.680°	a=18.0995 Å, c =30.0074 Å	a=20.1280 Å, b =13.3625 Å, c =21.5590 Å, β= 97.256°
Volume/ Å^3	1674.3	8509.4	5752.1
Z	2	3	4
Density (calculated)/g/cm^3	1.859	1.776	1.526
Absorption coefficient	1.621	1.761	0.990
F(000)	936.3	4538.9	2552.0
Crystal size	0.10×0.08×0.06 mm	0.12×0.12×0.05 mm	0.02×0.01×0.01 mm
Theta range for data	3.12– 25.03 °	4.28– 26.36 °	1.83– 25.03 °
Index ranges	-14≤ h ≤11;-15≤ k ≤ 13;-15≤ l ≤15	-22≤ h ≤22; - 22≤ k ≤ 22; -37≤ l ≤ 37	-21≤ h ≤23; - 15≤ k ≤ 15; -25≤ l ≤ 24
Reflections collected	11786	39485	20647
Independent reflections	5918	3863	4713
Completeness to θ_{max}	99.8%	99.6%	88.2%
Absorption correction	Gaussian	Gaussian	Multi-scan
T_{Max} and T_{min}	0.907 and 0.856	0.9171 and 0.8165	0.9795 and 0.9897
Refinement method	F^2	F^2	F^2
Data / restraints / parameters	5904/0/490	3863/1/240	4713/0/343
R_{int}	0.0448	0.0610	0.1336
Goodness-of-fit on F^2	1.070	1.072	0.975
Final R indices [I>2σ(I)]	0.0615	0.0674	0.0764
R indices (all data)	0.0824	0.0849	0.1051
Largest diff. peak and hole	0.691 and -1.984	1.048 and -1.264	1.071 and -0.781

2.2 Other Characterization

IR spectra were measured on A Varian 670-IR spectrometer with pure liquid or grounded crystalline samples. PXRD experiment was performed on a X'PertPANalytical PRO MRD using Cu Kα radiation (λ = 1.5418 Å) and variable divergence slits. Energy dispersion spectra were recorded on JEOL JSM-7000F schottky type FEG scanning electron microscope. The V/Zn ratio in SUT-12 is 2.8:1 (theoretical value 3:1). The V/Cu ratio in SUT-13 is 3.7:1 (theoretical value 4:1).

3. Molecular modelling

In order to investigate the binding energy of the different configuration of $Cu(DETA)_2^{2+}$, The geometry optimization of the $Cu(DETA)_2^{2+}$ with different configuration were optimized by using the first principle density functional theory (DFT) calculation. The geometric optimization is performed without any symmetry restriction. The numerical basis sets of double zeta quality plus polarization functions (DNP) were chosen for all calculations to describe the valence orbitals. The DFT semi-core pseudopods calculations (DSPP) were performed to treat the core electrons. As confirmed by other research on copper complex involved cases[4–6]. The RPBF exchange-correlation function based on the generalized gradient approximation (GGA) was employed to take account of the exchange and correlation effects of electrons. The complexation energy including relaxation can be determined through the binding energy difference of the reactant and product, which is denoted as $\triangle E = E_{\mathrm{product}} - E_{\mathrm{reactant}}$, for $Cu(DETA)_2$ complexes, and it can be expressed as $\triangle E_{\mathrm{binding}} = E_{\mathrm{Cu(DETA)2}^{2+}} - (E_{\mathrm{Cu}^{2+}} + 2E_{\mathrm{DETA}})$, *where* $E_{\mathrm{Cu(DETA)2}^{2+}}$, $E_{\mathrm{Cu}^{2+}}$ and E_{DETA} are the zero-point corrected energy of the optimized structure for $Cu(DETA)_2^{2+}$, Cu^{2+} and DETA respectively. The Binding energy for Cu^{2+} ion is 664.444 kcal/mol, which is similar to the reported value in ref 4. The binding energy for DETA is -1756.164 kcal/mol.

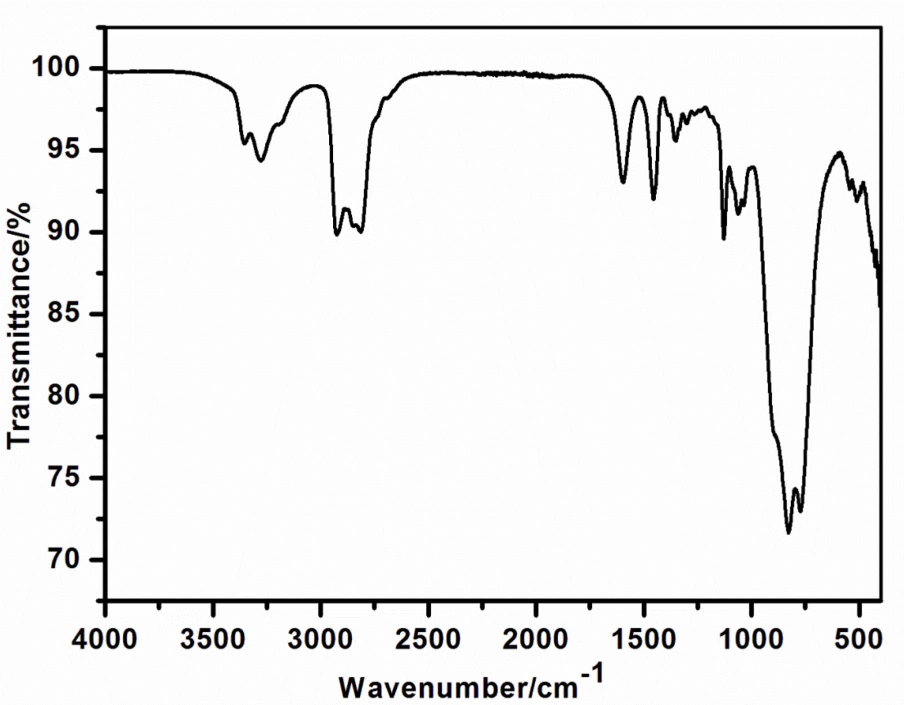

Figure S1. FT-IR spectrum of 99% DETA as purchased from Sigma-Aldrich. The band at 3361 cm^{-1} and 3278 cm^{-1} can be assigned to the symmetric stretching $\nu_s(NH_2)$ and the asymmetric stretching $\nu_{as}(NH_2)$ mode of amine groups. The bands corresponding to the symmetric stretching $\nu_s(CH_2)$ and asymmetric stretching bands $\nu_{as}(CH_2)$ of CH_2 group is located at 2926 cm^{-1} and 2815 cm^{-1}. The deformation and wagging oscillation of $\nu_d(NH)$ and $\nu_d(NH_2)$ of the amine groups are interpreted to be 1597 cm^{-1} and 1455 cm^{-1}. The deformation wagging oscillation of CH_2 and CH are shown at $\nu_d(CH_2)$ 1354 cm^{-1} and 1301 cm^{-1}. The stretching of CN (ν_{C-N}) and CC (ν_{C-C}) bonds appeared at 1128 cm^{-1} and 837 cm^{-1}, respectively.

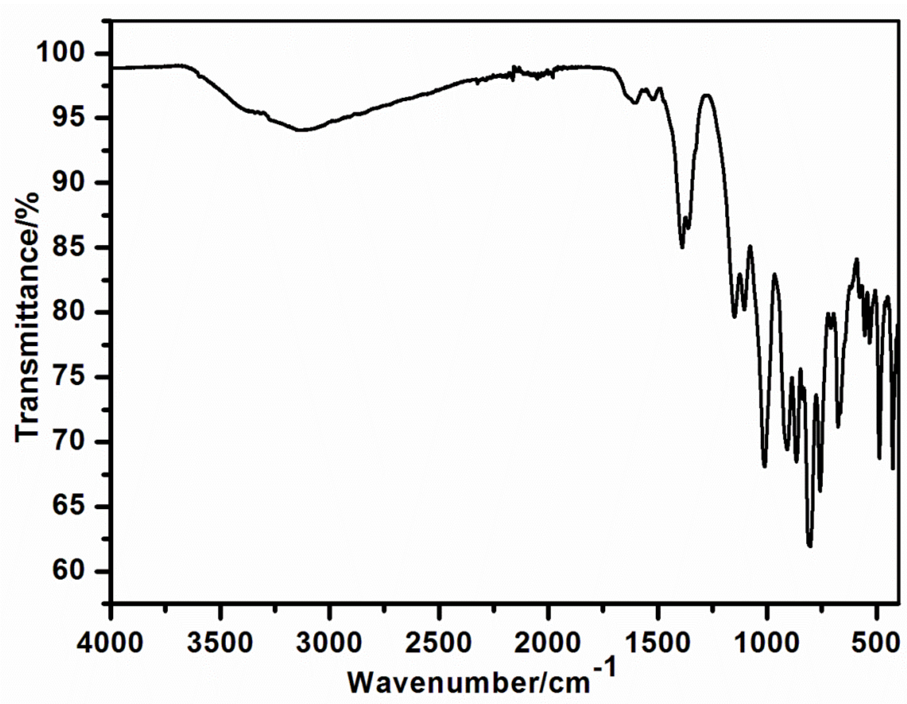

Figure S2. FT-IR spectrum of SUT-12. The CH_2, NH_2 and possible OH groups stretching mode were emerged in the broad band from 3613 cm^{-1} to 2400 cm^{-1}. But the deformation and wagging oscillation of ν_d(NH) and ν_d(NH_2) are clearly shown at 1607 cm^{-1}, 1520 cm^{-1} and 1476 cm^{-1}.

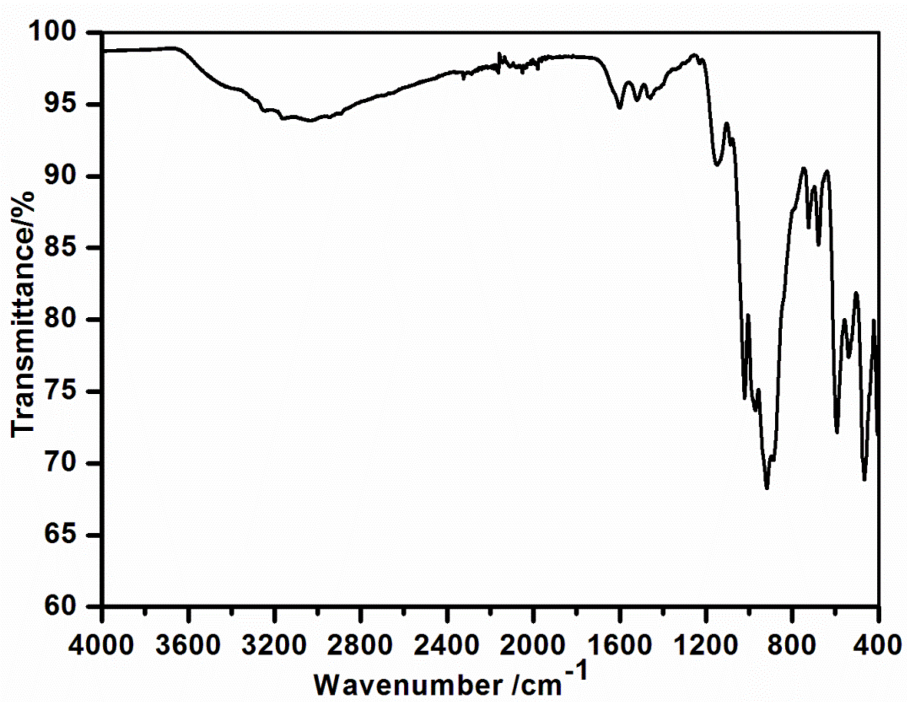

Figure S3. FT-IR spectrum of SUT-13. The CH_2, NH_2 and possible OH groups stretching mode were emerged in the broad band from 3634 cm^{-1} to 2377 cm^{-1}. But the deformation and wagging oscillation of ν_d(NH) and ν_d(NH_2) are clearly shown at 1599 cm^{-1}, 1521 cm^{-1} and 1459 cm^{-1}.

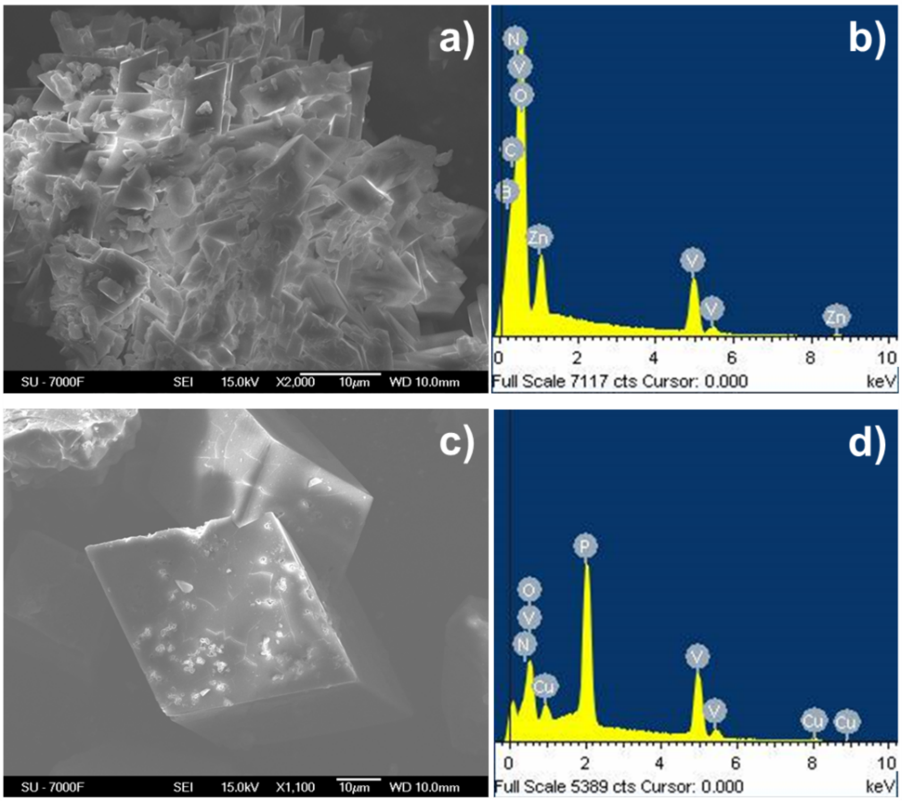

Figure S4. The scanning electron microscope image of a) SUT-12 and c) SUT-13; corresponding EDS spectra in b) and d).

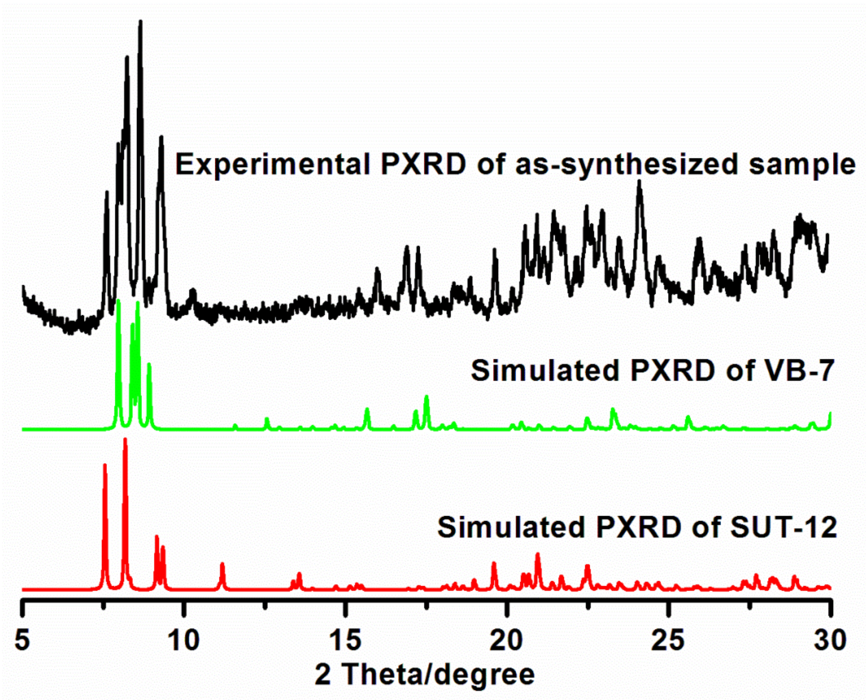

Figure S5. Powder X-ray diffraction pattern of SUT-12 and VB-7 mixture.

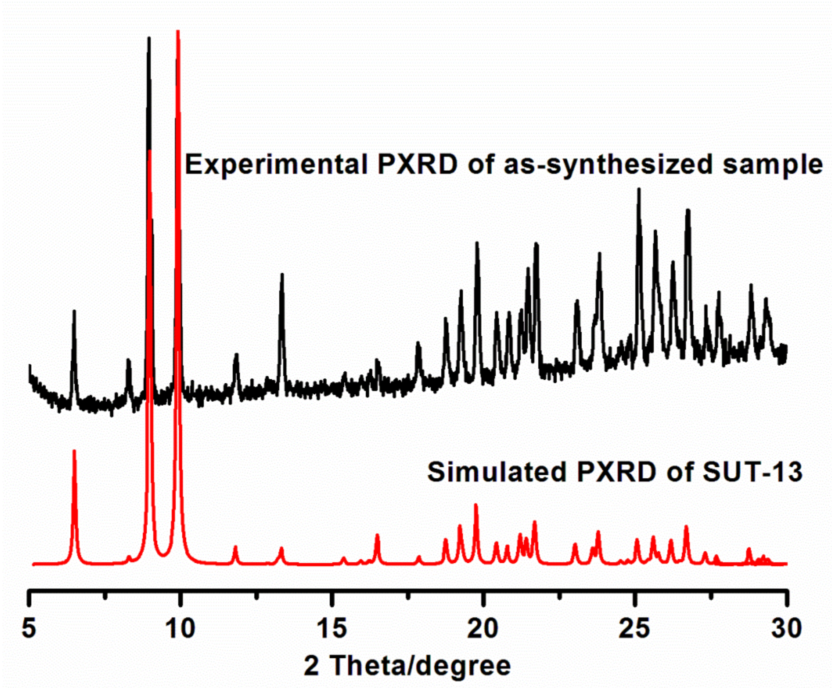

Figure S6. Powder X-ray diffraction pattern of SUT-13.

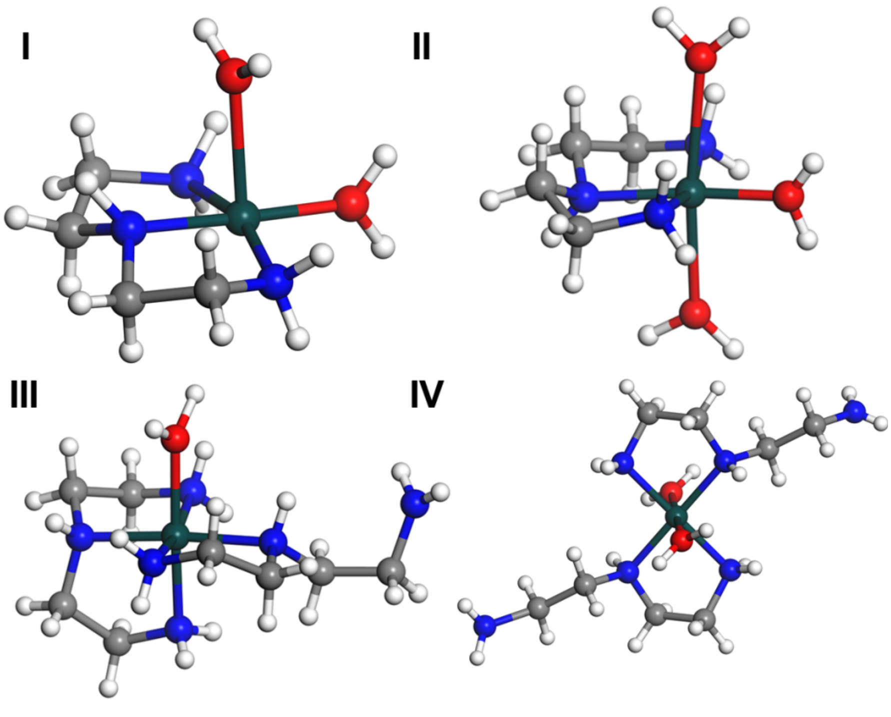

Figure S7. Different Cu-DETA-H_2O complexes used in DFT calculation. The model I and II are found in CCDC database; model III was built manually, and the DFT calculation shows that it cannot be converged during the geometry optimization process with the same parameters, which may indicate this configuration is energetically unfeasible in mono copper complexes; model IV is an analogue as in SUT-13. The calculated results including the different configurations of Cu(DETA)$_2$ are shown in Table S2.

Table S2. Complexation energy corresponding to different configurations of mono copper complexes.

Complex	$E_{binding}$(cal/mol)	Complexation energy (cal/mol)
Cu^{2+}	664444	
DETA	-1756164	
H_2O	-232254	
Figure 4-I	-3280597	-432713
Figure 4-II	-3278535	-430651
Figure 4-III	-3271174	-423290
Figure 4-IV	-3268394	-420510
Figure S7-I	-2131207	-574979
Figure S7-II	-2371907	-583425
Figure S7-IV	-3695913	-383521

References

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