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Supplementary information for

Chloride capturing system via proton-induced structure transformation between opened- and closed-forms of dodecavanadates

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Experimental Section

Instruments: NMR spectra were recorded with JEOL JNM-LA400. ^{1}H and ^{51}V NMR spectra were measured at 399.78 and 105.15 MHz, respectively. All spectra were obtained in the solvent indicated at 298 K. Chemical shifts were referenced to TMS (δ = 0 ppm) for ^{1}H NMR and $VOCl_3$ (δ = 0 ppm) for ^{51}V NMR. IR spectra were measured on Jasco FT/IR-4100 using KBr pellet or nujol methods. Electrospray ionization mass (ESI-MS) spectra in negative mode were recorded on a micromass LCT mass spectrometer. An acetonitrile solution was directly injected at the flow rate of 400 μL/min. Elemental analyses of C, H, and N were performed by the Research Institute for Instrumental Analysis at Kanazawa University. Elemental analysis of Cl was performed by the Center for Organic Elemental Microanalysis Laboratory at Kyoto University. GC analysis was performed on Shimadzu GC-2014 with a flame ionization detector (FID) equipped with a ZB-WAXplus capillary column (phenomenex, internal diameter = 0.25 mm, length = 30 m). Naphthalene was used as the internal standard. An ALS/CH Instruments electrochemical analyzer (Model 600A) was used for voltammetric experiments. The working electrode was glassy carbon, the counter electrode was Pt wire, and the reference electrode was Ag/Ag^{+}. The voltage scan rate was set at 100 mV s^{-1}. The potentials in all voltammetric experiments were converted using data derived from the oxidation of Fc (Fc/Fc^{+}, Fc=ferrocene) as an external reference.

Reagents: Solvents and benzaldehyde were obtained from Wako. Diethylamine and malononitrile was obtained from TCI. Ethylenediamine and CF_3COOH were obtained from Wako and TCI, and used after the dilution to 47 and 110 mM solution with acetonitrile and nitromethane, respectively. $\{Et_4N\}Cl$ (TEACl) and $AgBF_4$ were obtained from TCI and used after the dilution to 94 and 110 mM solution with acetonitrile, respectively. TEA salt of **opened-V12**, and tetra-*n*-butylammonium (TBA) salt of **closed-V12** were synthesized by the reported procedures.[7]

X-ray Crystallographic analysis: Single crystal structure analysis was performed at 90 K by using a Rigaku/MSC Mercury diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71069 Å) and with 0.5° ω-scans at 0° and 90° in φ. The crystal data is summarized in Table S1. Data were collected and processed by using the CrystalClear program [S1]. Numerical absorption corrections were applied by using CrystalClear and corrections for Lorenz and polarization effects were performed. The structure analysis was performed using CrystalStructure [S2]. All structures were solved by SHELXS-2013 (direct methods) and refined by SHELXL-2013 [S3,S4]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms are positioned geometrically and refined using a riding model.

Transformation of closed-V12 to opened-V12: All reactions and manipulations were conducted under a nitrogen atmosphere. To an acetonitrile solution of TBA salt of **closed-V12** $TBA_4[HV_{12}O_{32}(Cl)]$ (9.4 mM, 1 mL), diluted ethylenediamine (47 mM, 0.1 mL) and TEACl (94 mM, 0.1 mL) were added. The solution was stirred at room temperature for 4 days. The imperceptible organic white precipitates formed were removed by filtration. After addition of a large amount of diethyl ether to the clear solution yielded precipitates. They were collected by filtration (90% yield based on V). Anal. Calcd for $TBA_3TEA\{(CH_2)_2(NH_3)_2\}_{0.5}[V_{12}O_{32}(Cl)]$: C, 33.44; H, 6.55; N, 3.42; found: C, 33.82; H, 6.69; N, 3.40. IR (KBr; 1100-400 cm^{-1}): 989, 854, 788, 759, 710, 645, 605, 544, 515 cm^{-1}. ^{51}V NMR (acetonitrile): $\delta = -583, -589, -599$ ppm.

Transformation of opened-V12 to closed-V12: All reactions and manipulations were conducted under a nitrogen atmosphere. To a nitomethane solution of TEA salt of **opened-V12** $TEA_5[V_{12}O_{32}(Cl)]$ (5.5 mM, 2 mL), diluted CF_3COOH (110 mM, 0.1 mL) were added. The solution was stirred at room temperature for 8 days. The precipitates formed after addition of large amount of diethyl ether were collected by filtration (92% yield based on V). Anal. Calcd for $TEA_4[HV_{12}O_{32}(Cl)]$: C, 22.87; H, 4.86; N, 3.33; found: C, 23.15; H, 4.92; N, 3.33. IR (KBr; 1100-400 cm^{-1}): 989, 872, 827, 781, 714, 683, 665, 629, 580, 527 cm^{-1}. ^{51}V NMR (nitromethane): $\delta = -540, -565, -573, -575, -626$ ppm.

Synthesis of $TBA(Et_2NH_2)_4[V_{12}O_{32}(Cl)]$ (tube-V12): To a dichloromethane solution of TBA salt of **closed-V12** $TBA_4[HV_{12}O_{32}(Cl)]$ (9.5 mM, 20 mL), diethylamine hydrochloride (260 mg, 2.4 mmol) and diethylamine (99 mM, 1.9 mL) were added. After the stirring overnight at 313 K, brown precipitates formed were removed by filtration and the filtrate was concentrated to ca, 10 mL under reduced pressure. After addition of diethyl ether (50 mL) to the solution, the yellow precipitates formed were collected by filtration. The collected samples were dissolved in chloroform (40 mL) and insoluble materials were removed by filtration. After standing the filtrate overnight, the yellow products of $TBA(Et_2NH_2)_4[V_{12}O_{32}(Cl)]$ were collected by filtration (193 mg, 60% yield based on V). Single crystals suitable for X-ray analysis were obtained from the mixed solvent of acetonitrile and ethyl acetate at room temperature (Table S1). Anal. Calcd for $TBA(Et_2NH_2)_4[V_{12}O_{32}(Cl)]$ C, 22.64; H, 4.99; N, 4.13; Cl, 2.09 found: C, 22.50; H, 5.17; N, 4.08; Cl, 2.11. IR (KBr; 1100-400 cm^{-1}): 989, 975, 964, 878, 820, 771, 685, 656 cm^{-1} (Fig. S11). ^{51}V NMR (acetonitrile): $\delta = -559, -584$ ppm (Fig. S2). ^1H NMR (acetonitrile-d_3): δ = 6.53 (8H, Et_2NH_2), 3.08 (8H, TBA), 3.03(16H, Et_2NH_2), 1.59 (8H, TBA), 1.34 (8H, TBA), 1.32 (24H, Et_2NH_2), 0.94 (12H, TBA) ppm (Fig. S2). ESI-MS (1 mM, acetonitrile): m/z = 386.7 ($\{H_2[V_{12}O_{32}(Cl)]\}^{3-}$), 580.1 ($\{H_3[V_{12}O_{32}(Cl)]\}^{2-}$), 617.0 ($\{(Et_2NH_2)H_2[V_{12}O_{32}(Cl)]\}^{2-}$). CCDC 1440817 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Reaction of closed-V12 with $AgBF_4$: To an acetonitrile solution of TBA salt of **closed-V12** (55 mM, 6 mL) $AgBF_4$ (110 mM 3 mL) was added. No precipitates were formed. The precipitates of $TBA_3Ag[HV_{12}O_{32}(Cl)]$ formed after addition of large amount of diethyl ether were collected by filtration, washed by small amount of diethyl ether, and dried (92% yield based on V). Anal. Calcd for $TBA_3Ag[HV_{12}O_{32}(Cl)]$: C, 29.35; H, 5.72; N, 2.19; Cl,1.68; found: C, 28.90; H, 5.51; N, 2.21; Cl, 1.78. IR (KBr; 1100-400 cm^{-1}): 997, 878, 819, 763, 722, 697, 669, 612, 565, 530 cm^{-1} (Fig. S5). ^{51}V NMR (acetonitrile): $\delta = -531, -541, -558, -568, -578, -622$ ppm (Fig. 7, S6). ESI-MS: m/z = 755.2 ($\{TBA[AgHV_{12}O_{32}(Cl)]\}^{2-}$), 436.4 ($\{Ag[HV_{12}O_{32}(Cl)]CH_3CN\}^{3-}$), 422.7 ($\{Ag[HV_{12}O_{32}(Cl)]\}^{3-}$) (typical peaks) (Fig. 6).

Reaction of opened-V12 with $AgBF_4$: To an acetonitrile solution of TEA salt of **opened-V12** (1.1 mM, 20 mL), $AgBF_4$ (110 mM 0.2 mL) was added. The white precipitates of AgCl formed were removed by filtration. The filtrate was evaporated to ca. 10 mL. The precipitates of $TEA_4[V_{12}O_{32}]$ (TEA salt of **opened-V12’**) formed after addition of large amount of diethyl ether were collected by filtration, washed by small amount of water and diethyl ether, and dried (89% yield based on V). Anal. Calcd for $TEA_4[V_{12}O_{32}]$: C, 23.22; H, 4.87; N, 3.75; Cl,0.00; found: C, 23.37; H, 4.90; N, 3.41; Cl, 0.00. IR (KBr; 1100-400 cm^{-1}): 992, 860, 787, 761, 711, 649, 615, 548, 521 cm^{-1}. ^{51}V NMR (acetonitrile): $\delta = -589, -597, -605$ ppm (Fig. 7).

Additional references:

[S1] CrystalClear, version 1.3.5, Rigaku Corporation, Tokyo, Japan.

[S2] CrystalStructure, version 4.1, Rigaku Corporation, Tokyo, Japan.

[S3] G. M. Sheldrick, *Acta Cryst.* 2008, **A64**, 112-122.

[S4] G. M. Sheldrick, *SHELXL2013.* University of Göttingen, Germany, 2013.

Table S1. Crystallographic data for $TBA_2(Et_2NH_2)_8[V_{12}O_{32}(Cl)]_2(EtOAc)_2CH_3CN$

formula	$C_{74}H_{190}Cl_2N_{11}O_{68}V_{24}$
fw	3612.83
cryst syst	Monoclinic
space group	*C*2/*c* (No. 15)
a (Å)	50.145(9)
b (Å)	11.7630(18)
c (Å)	24.476(4)
β (deg)	105.706(4)
V (Å^3)	13898(4)
Z	4
μ (mm^{-1})	1.655
no. of params refined	822
*R*1 ($I > 2\sigma(I)$)	0.0705 (for 13234 data)
*wR*2	0.1917 (for all 15672 data)

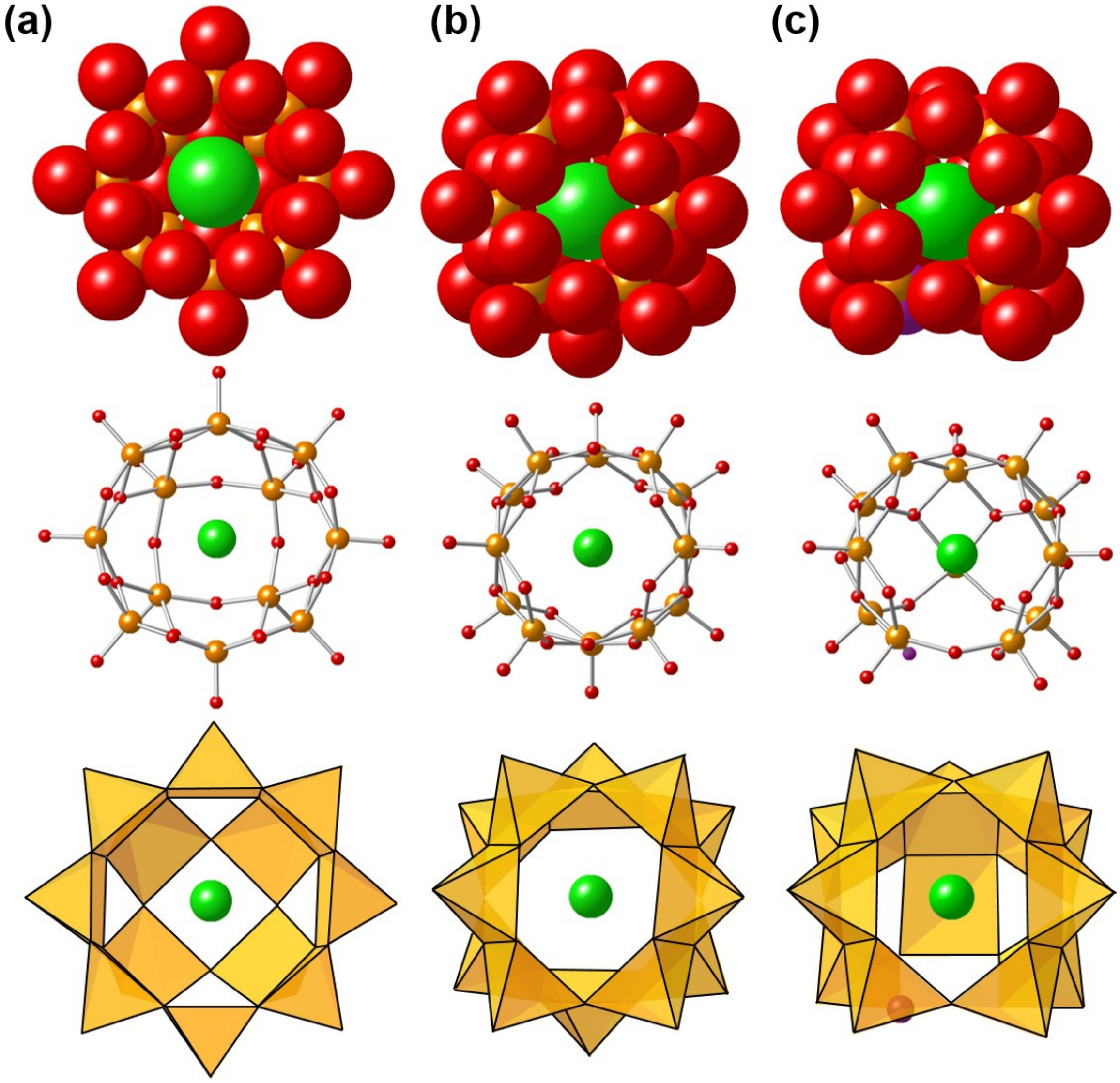

Fig. S1 Space-filling, ball-and-stick and polyhedral representations of (a) **opened-V12**, (b) **tube-V12** and (c) **closed-V12**. Green, yellow, red and purple spheres represent chlorine, vanadium, oxygen and protonated-oxygen atoms, respectively. Square-pyramids represent VO_5 units. Only **opened-V12** has a cavity accessible by external reagents.

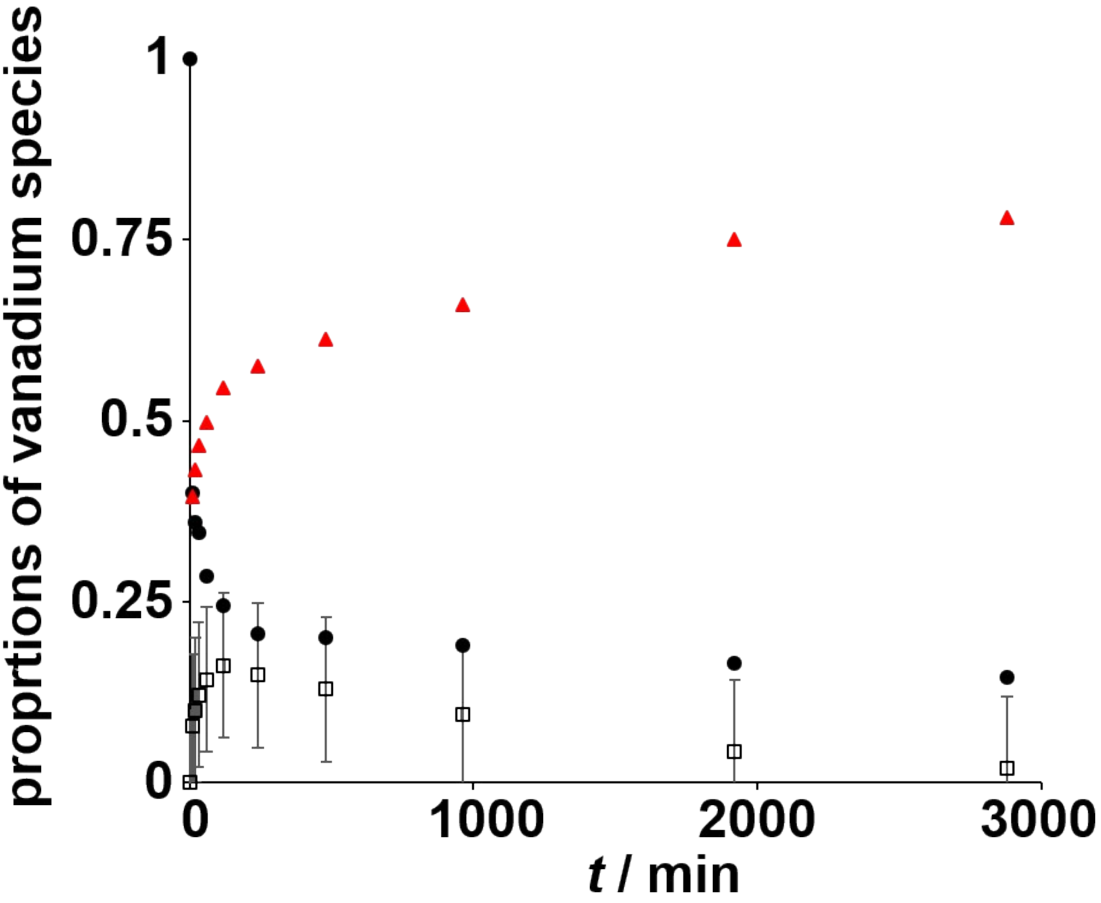

Fig. S2 Time dependent observation of the proportions of vanadium species determined by ^{51}V NMR spectra in the initial stage of the transformation of **closed-V12** to **opened-V12**. Circles, triangles and squares represent the ratio of **closed-V12**, **opened-V12** and **tube-V12**, respectively.

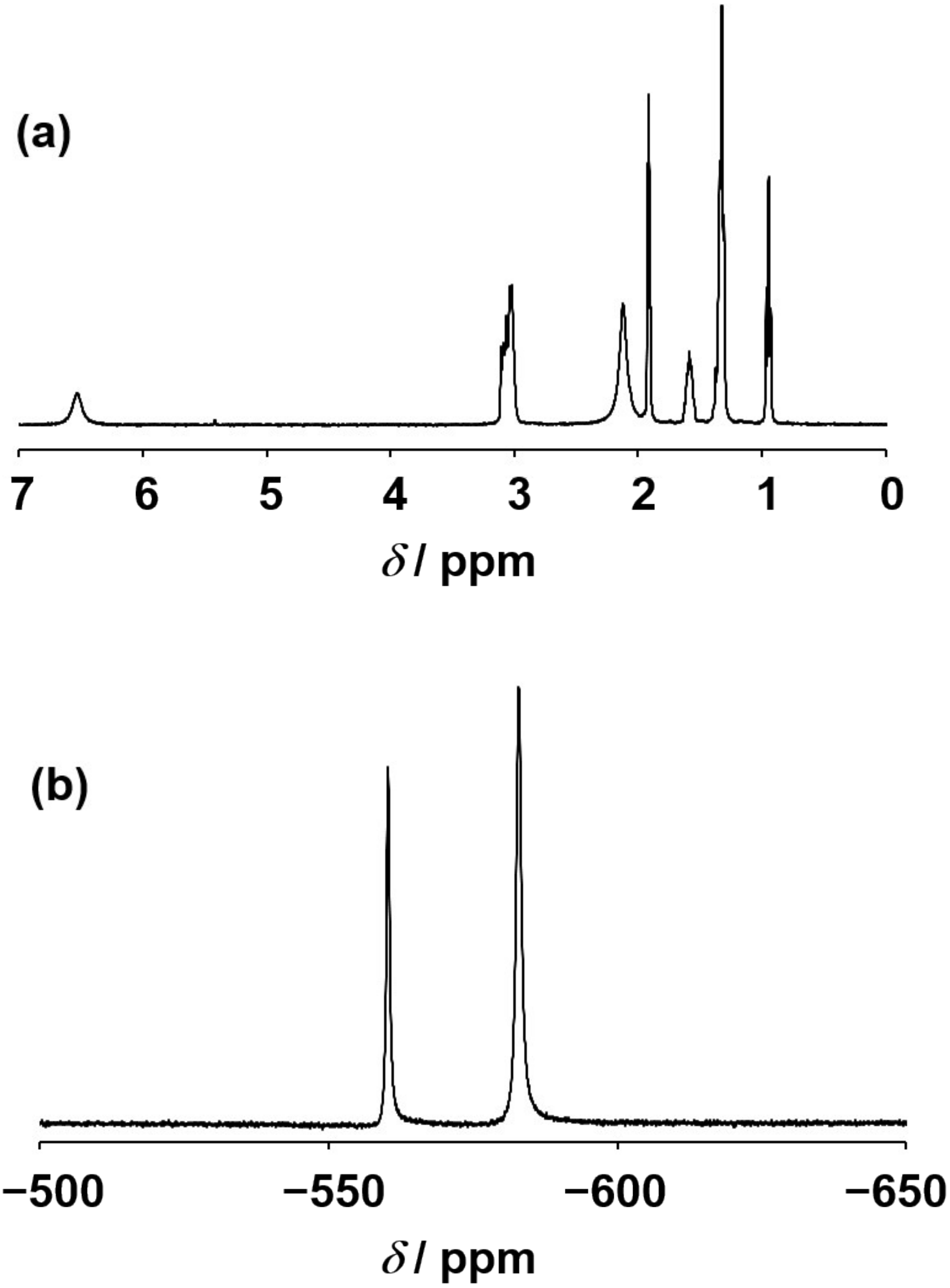

Fig. S3 (a) ^{1}H and (b) ^{51}V NMR spectra of TBA$(Et_2NH_2)_4[V_{12}O_{32}(Cl)]$ in CD_3CN.

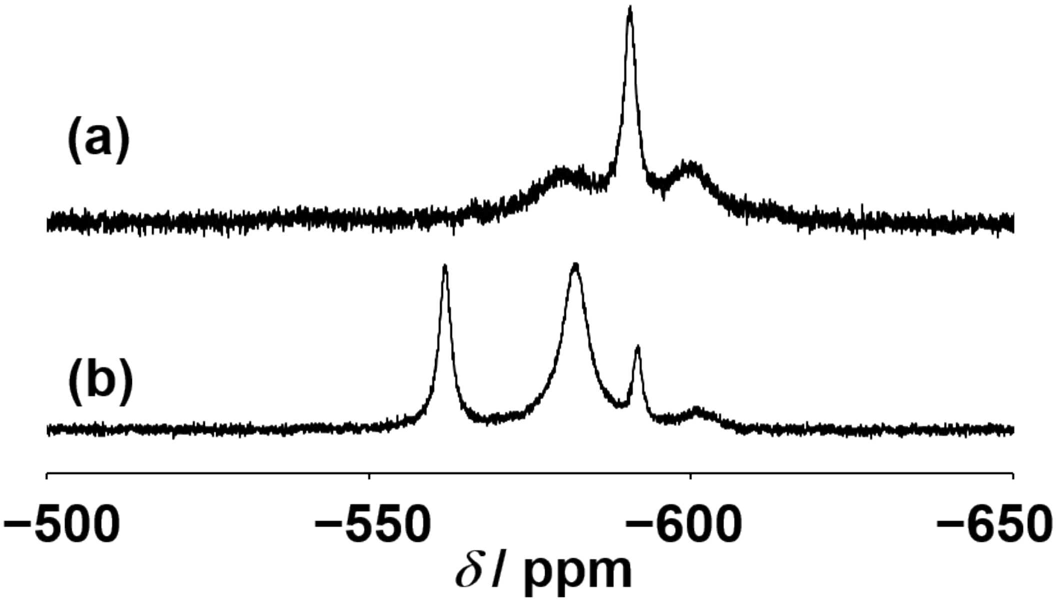

Fig. S4 ^{51}V NMR spectra of the reaction solution of (a) **tube-V12** with 200 equivalents of {Et_4N}Cl, and (b) **opened-V12** with 200 equivalents of (Et_2NH)HCl, in the mixed solvent of propylene carbonate and chloroform (1:1.5, v/v) at 303 K for 3 days. The transformation of **tube-V12** to **opened-V12** completely proceeded, while the yield of reverse reaction reached only ca. 85% partly due to the thermodynamic stability of **opened-V12**. Low S/N ratio in (a) was due to the low solubility of **opened-V12** under this condition.

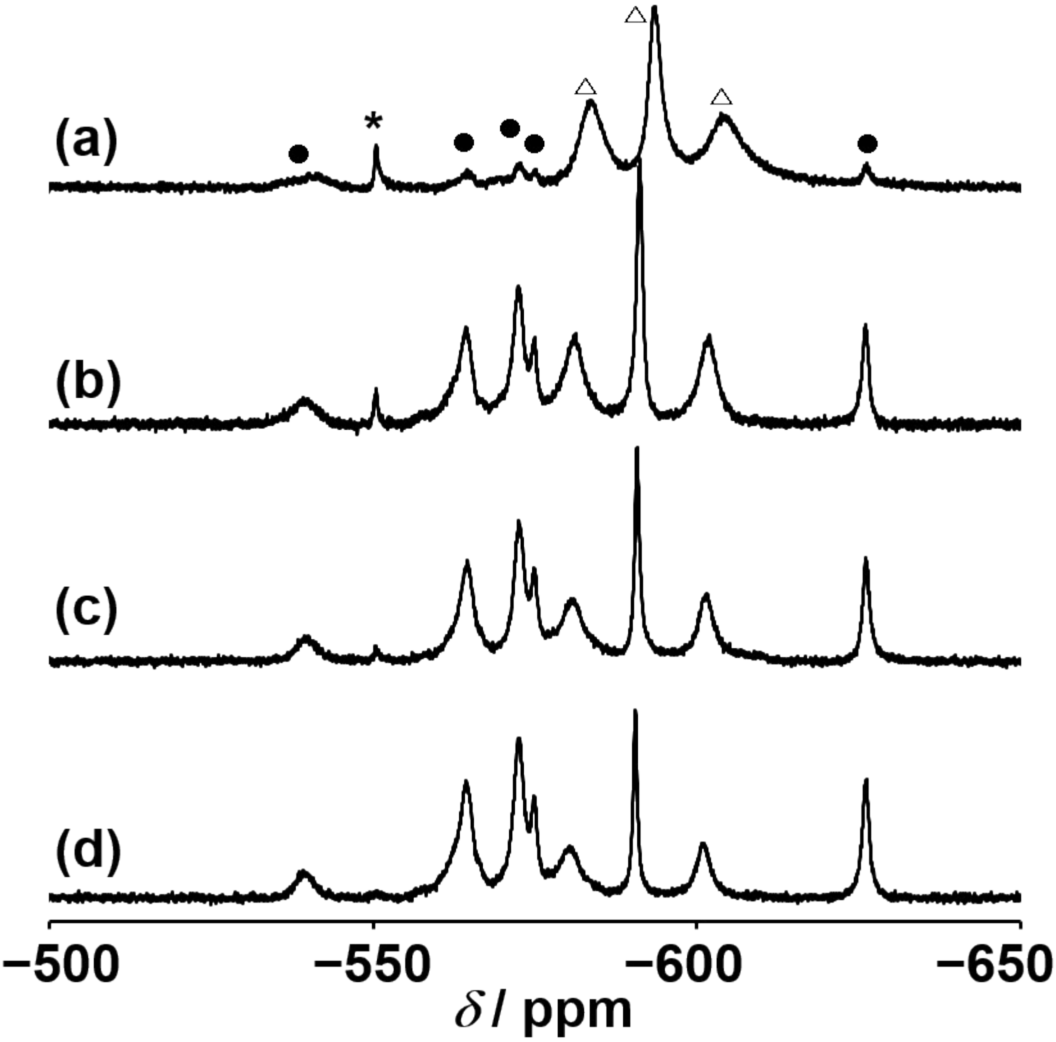

Fig. S5 ^{51}V NMR spectra of **opened-V12** in acetonitrile in the presence of 1.0 equivalent of CF_3COOH after (a) 1 h, (b) 6 h, (c) 12 h and (d) 24 h in an NMR sample tube. Asterisks, circles and triangles represent the peaks assignable to an intermediate, **closed-V12** and **opened-V12**, respectively.

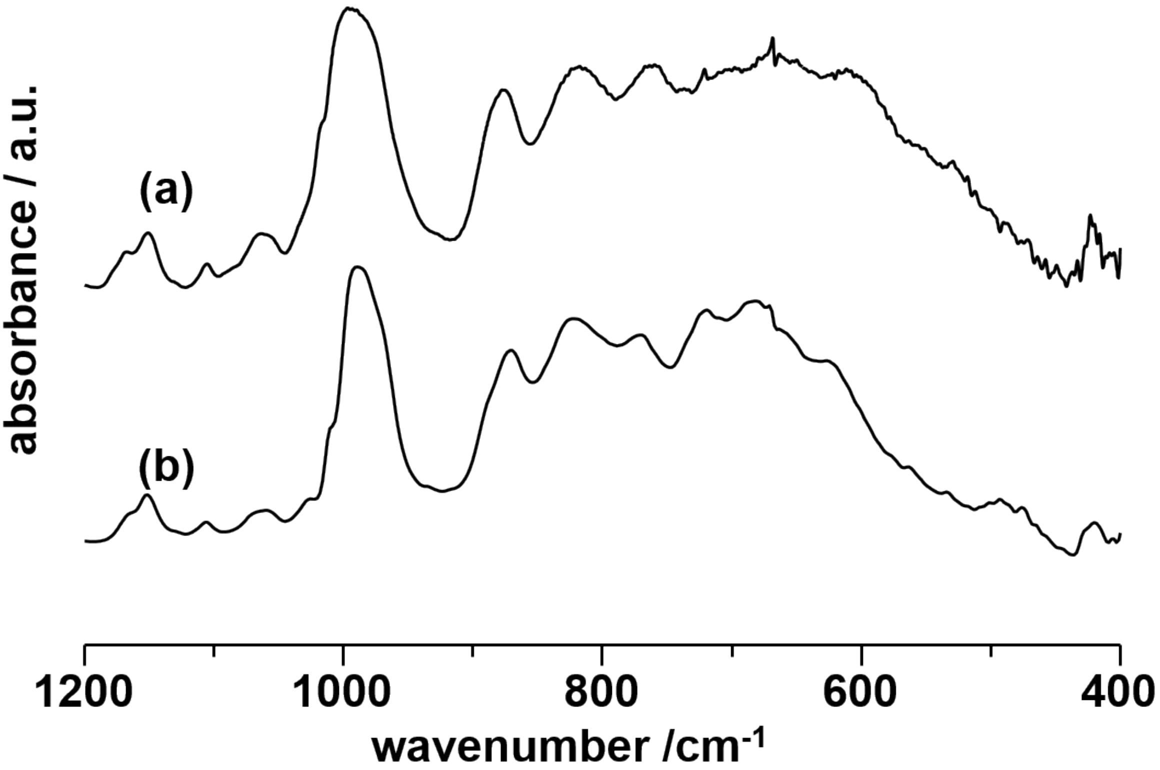

Fig. S6 IR spectra of (a) the sample obtained after the reaction of **closed-V12** with 1.0 equivalent of $AgBF_4$ and (b) the authentic samples of **closed-V12**, using a nujol method.

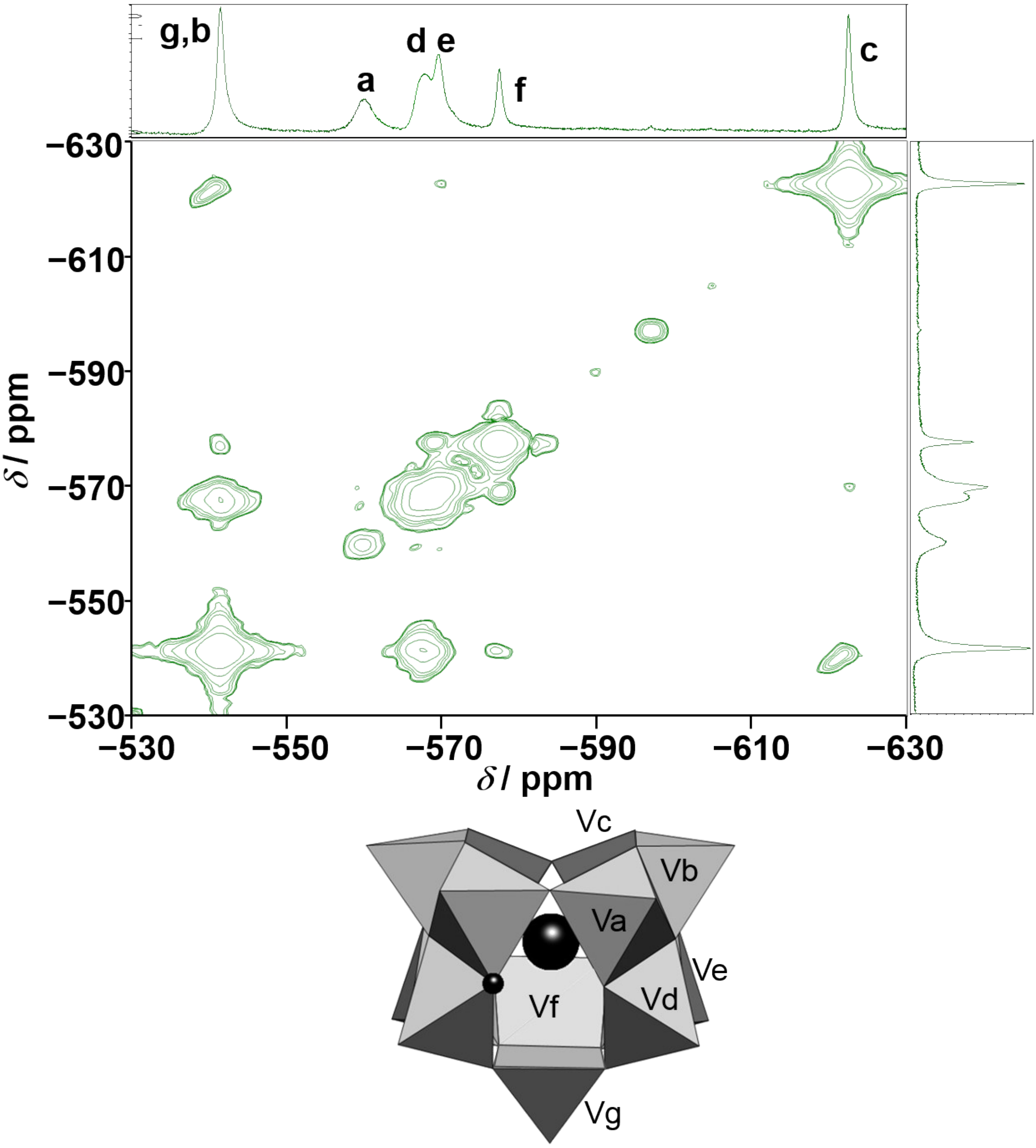

Fig. S7 ^{51}V-^{51}V COSY spectrum of **closed-V12’** in acetonitrile-d_3.

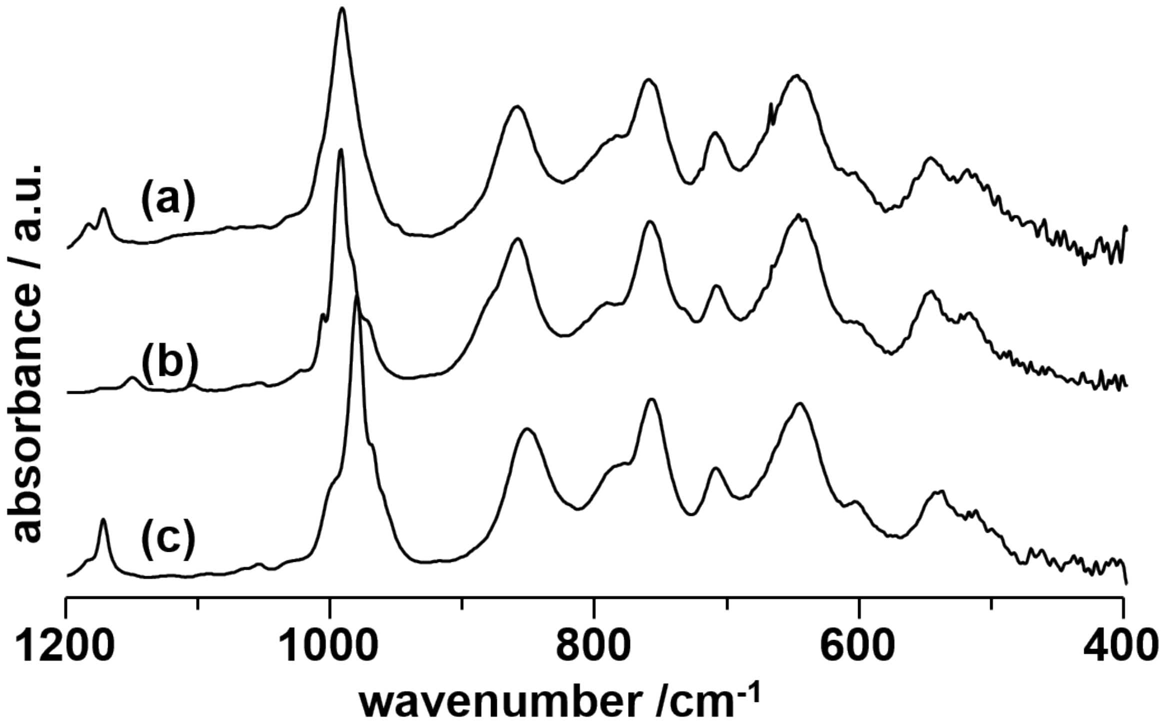

Fig. S8 IR spectra of (a) the sample obtained after the reaction of **opened-V12** with 1.0 equivalent of AgBF$_4$, (b) the authentic sample of **opened-V12'** and (c) the authentic sample of **opened-V12**.

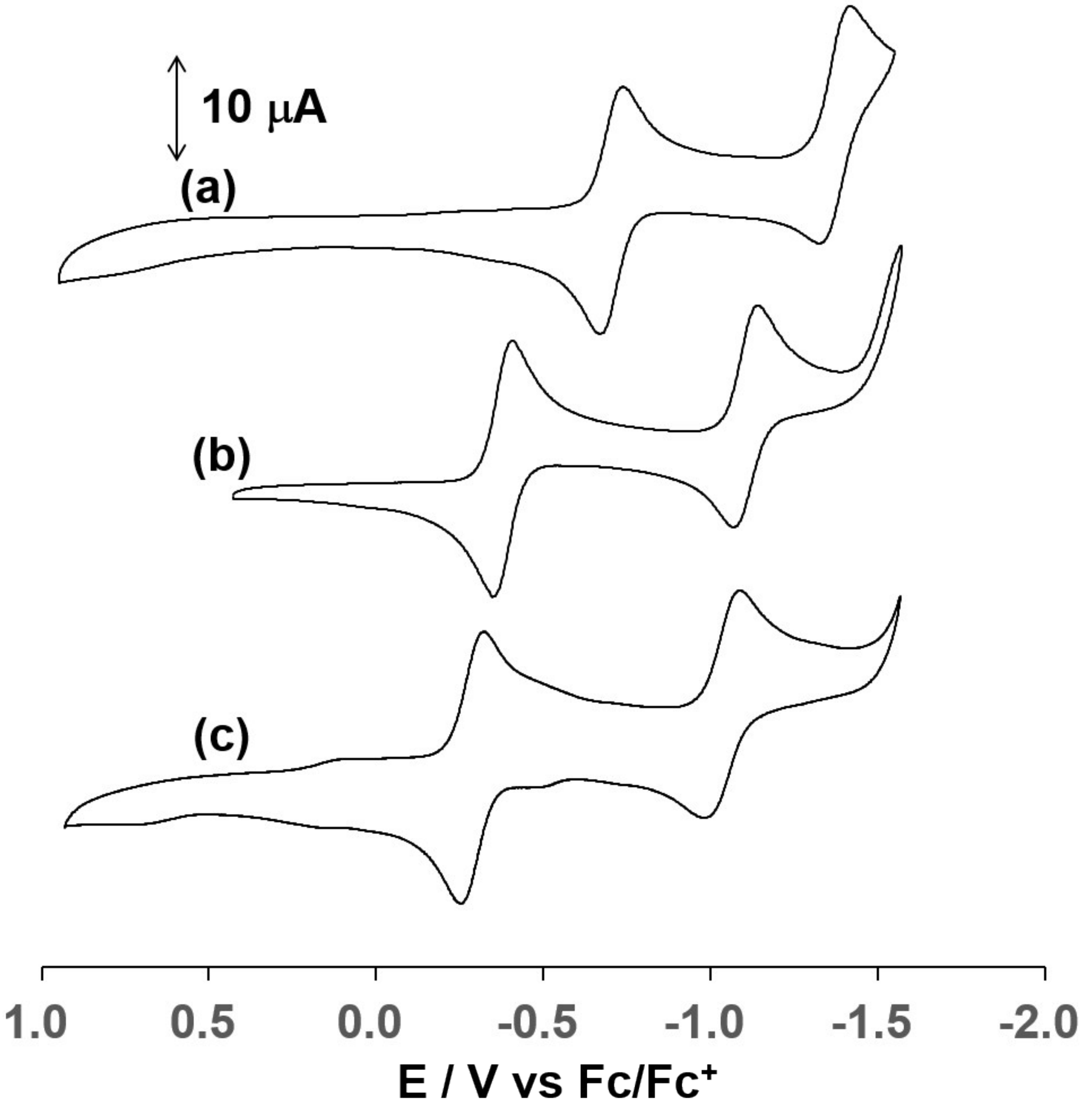

Fig. S9 Cyclic voltammograms of (a) **opened-V12**, (b) **opened-V12’** and (c) **closed-V12** in acetonitrile. Scan rate was 0.1 V/sec. The supporting electrolyte was $\{n\text{-Bu}_4\text{N}\}\text{PF}_6$.

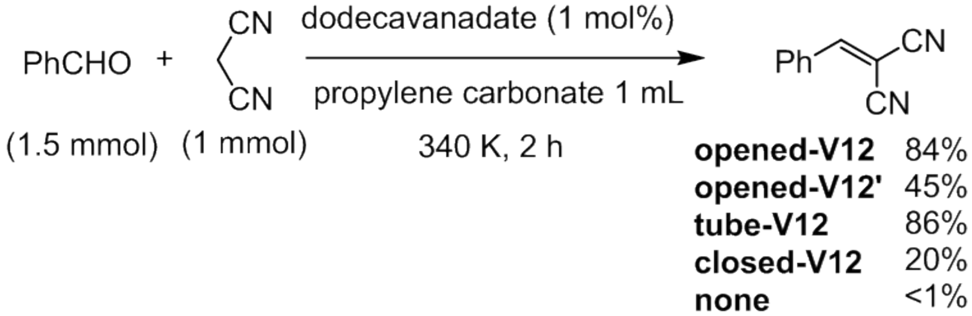

Fig. S10 The Condensation of benzaldehyde with malononitrile.

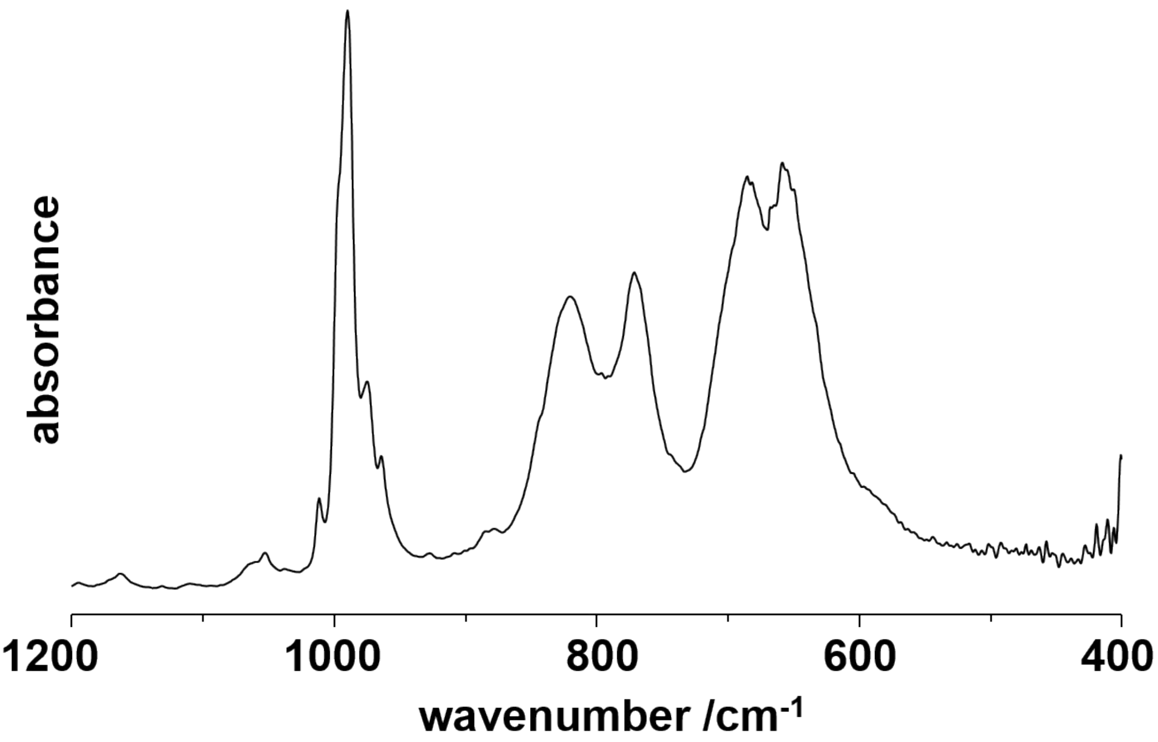

Fig. S11 IR spectrum of **tube-V12**.