Supporting Information

A Microporous Titanosilicate for Selective Killing of HeLa Cancer Cells

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Scanning electron microscopy and energy-dispersive X-ray spectroscopy *(SEM/EDS).* The SEM images and chemical analyses of Zn-ETS-4 and Zn-STS were realized with NanoSEM - FEI Nova 200 (FEG/SEM) - EDAX - Pegasus X4M (EDS/EBSD) and the ones of CPT with Zeiss LS 25. Data of the chemically analyzed ion exchanged crystals are shown on Table S1. ETS-4 crystallizes as prismatic 20 μm particles and as 80 μm single crystals mixed with GTS-1 (Figure S1)[1-3]. STS was prepared in its typical morphology of small 15μk hexagon-like crystals (Figure S1)[4].

The natural CPT appeared as shapeless mass and prismatic single crystals with maximum length of 15 μk (**FigureS1**).

Table S1. Chemical composition of the Zn-exchanged solids.

	Zn-ETS-4		Zn-STS		Zn-CPT	
Atom	Refinement	EDS ratio	Refinement	EDS ratio	Refinement	EDS ratio
Si	12	12.11	3	3.24	30	29.62
Ti	5	4.77	1	0.91	-	-
Al	-	-	-	-	6	6.32
K	-	0.04	1.16	1.55	0.4	0.41
Na	-	-	-	-	0.2	0.19
Zn	3.12	5.21	0.42	0.55	2.21	2.19
Ca	-	-	-		0.4	0.39
Mg	-	-	-	-	0.2	0.2

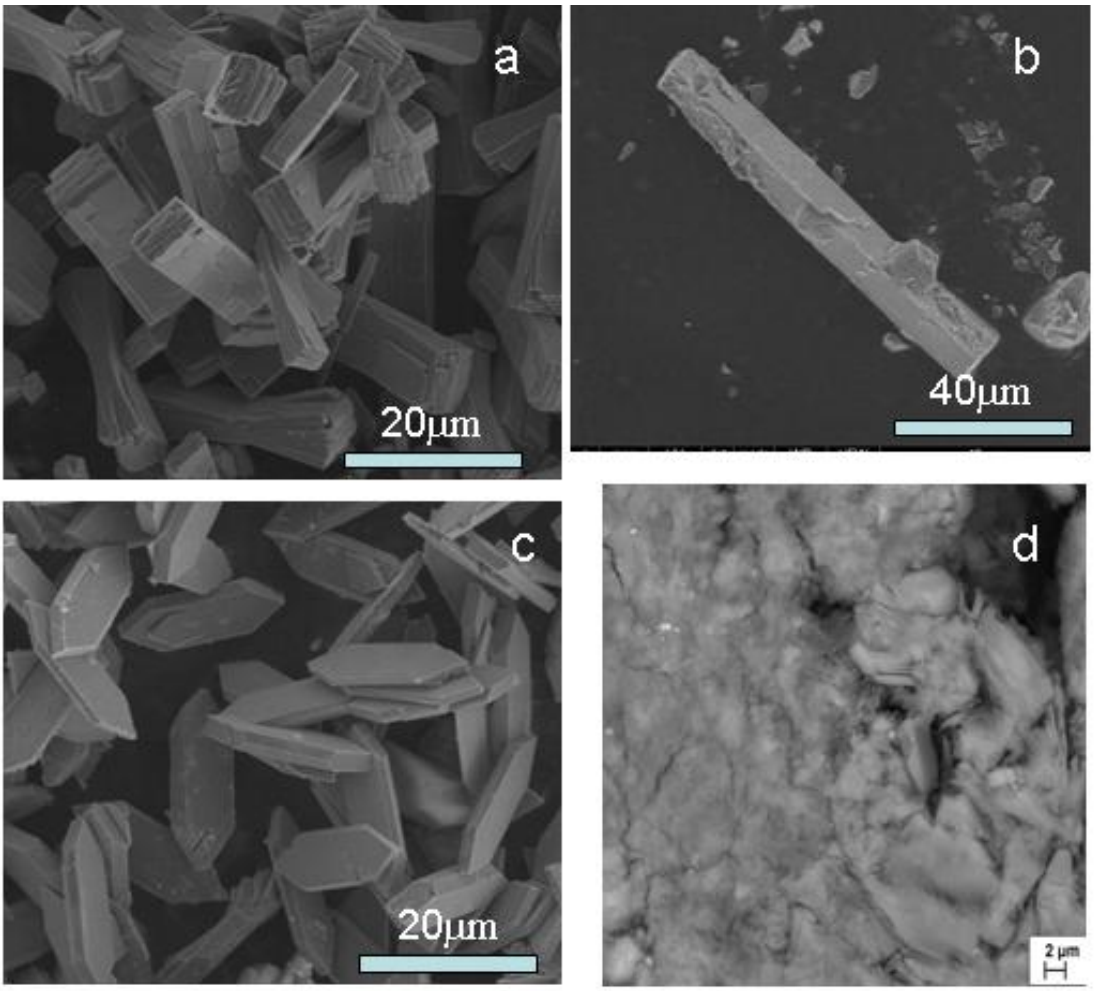

Figure S1. SEM images of Zn-exchanged ETS-4 (a, b), STS (c) and CPT (d).

Thermogravimetry (TG) analysis. The TG curves were collected with a Shimadzu TG-50 (Zn-ETS-4 and Zn-STS; heated in air at the rate of 5 °C min^{-1}) and Stanton Redcroft (Zn-CPT heated in argon at the rate of 5 °C min^{-1}) analyzers (**Figure S2**).

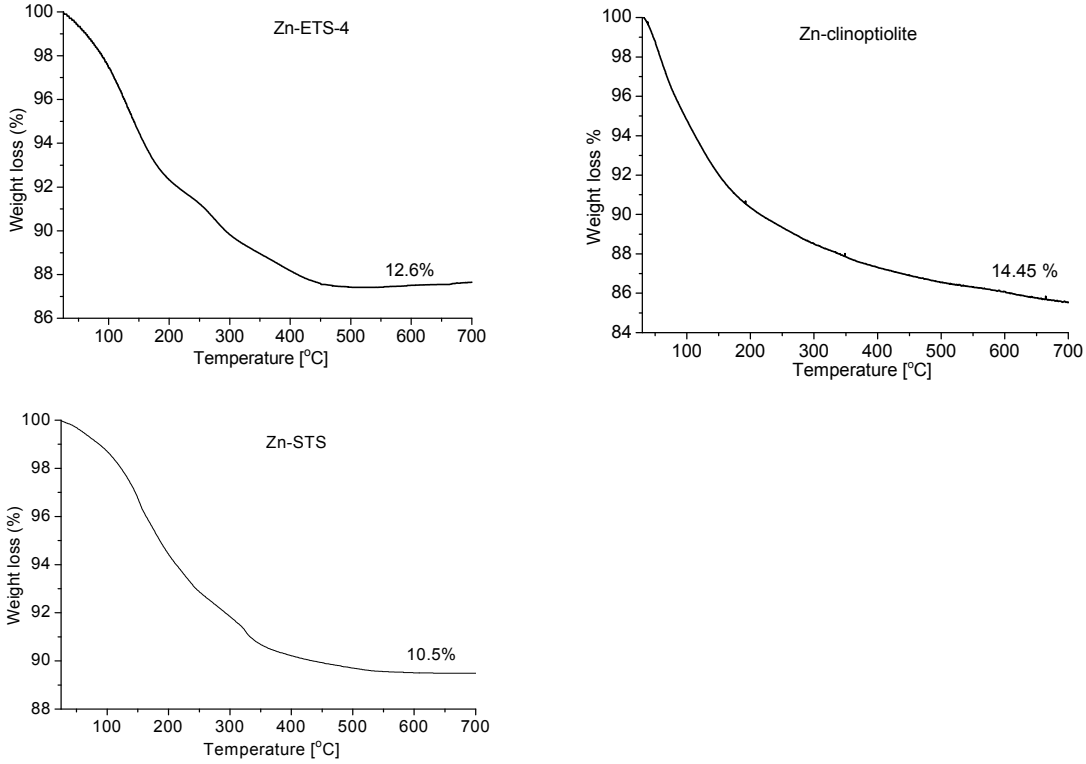

Figure S2. TG curves of Zn-exchanged molecular sieves.

Powder X-ray diffraction. The powder XRD analyses were performed on a Bruker D8 Discover (Zn-ETS-4 and Zn-STS) and Bruker D8 Advance (Zn-CPT) diffractometers. For the structural analysisof Zn-STS the pattern was collected in $\theta/2\theta$ scan regime, using CuKα radiation, λ=1.54060 Å, step 0.02°, time per step 20 s, 2θ range 9–100°. The data for the Zn-CPT were collected in $\theta/2\theta$ scan regime, using CuKα radiation, step 0.02°, time per step 10 s, 2θ range 8–100°. The Rietveld refinement wascarried out by TOPAS-3 software package[5] applying the fundamental parameters approach (FPA)[6]. In the profile-fitting process of the FPA[6], the intensity profile is derived from the X-ray emission profile, instrument parameters and specimen dependent parameters. The set of diffractometer-dependent variables were used with a full axial divergence model. The refined specimen-dependent parameters were the zero error and the background (Chebyshev polynomial fitting).

The starting model for the Rietveld refinement was the Na-exchanged form of titanium umbite[7]. and previous single crystal data of the mineral clinoptilolite[8]. Once profile fitting was completed the framework atomic coordinates were refined. Next, the cations and water positions were refined until least squares refinement converged. The cation sites and water molecules occupancies were freely refined while isotropic thermal factors were held constant. The elements were assigned to the extra-framework sites on the basis of electron density, distances to framework atoms, distances to other channel occupants, charge balance, and exchange ratios as determined by ICP-OES[9] and confirmed by EDS and TG analyses. Crystallographic details from the Rietveld refinement, atomic coordinates, isotropic parameters and selected interatomic distances are shown in Tables S2-S7. The observed, calculated, and difference profiles are given in Figures S3 and S4. The powder XRD pattern of the Zn-exchanged ETS-4

Table S2. Crystal data and Rietveld refinement parameters of Zn-STS

compound	Zn-STS $K_{1.16}Zn_{0.42}TiSi_3O_9 \cdot 2H_2O$
formula weight	1469.96 g/mol
crystsyst	monoclinic
space group (No.)	$P2_1/c$ (14)
unit cell	a=7.205(9), b=10.034(2), c=12.89(4) Å, β=91.5(1)°
volume	931.9(9) $Å^3$
D(calcd)	2.6189(1) g/cm^3
No. reflections	970
Reliability factors	R_p = 8.25, R_{wp} = 11.08, R_{exp} = 4.44, χ^2 = 2.49
structure factor	R_B = 4.31

Table S3. Atomic coordinates, occupancies and isotropic displacement parameters for Zn-exchanged STS.

Atom	x	y	z	Occ.	*B* (Å^2)
Ti1	0.2600(1)	0.7054(2)	0.205(6)0	1	1.46(9)
Si1	0.012(7)	0.432(6)	0.1733(4)	1	1.56(9)
Si2	0.7225(9)	0.296(2)	0.0420(3)	1	1.56(9)
Si3	0.421(1)	0.40(4)	0.171(4)	1	1.56(9)
O1	0.244(9)	0.681(6)	0.36(4)	1	1.92(3)
O2	0.041(7)	0.591(5)	0.189(7)	1	1.92(3)
O3	0.257(1)	0.756(2)	0.066(8)	1	1.92(3)
O4	0.477(7)	0.822(4)	0.233(8)	1	1.92(3)
O5	0.087(9)	0.864(9)	0.225(9)	1	1.92(3)
O6	0.428(1)	0.561(8)	0.19(5)	1	1.92(3)
O7	0.204(9)	0.3600(1)	0.156(7)	1	1.92(3)
O8	0.521(9)	0.365(9)	0.063(2)	1	1.92(1)
O9	0.880(4)	0.411(4)	0.073(4)	1	1.92(1)
K1	0.7449(6)	0.6989(2)	0.0990(8)	1	3.86(9)
Zn1/K2	0.314(8)0	0.4311(2)	0.6060(5)	0.42/0.16	5.71(3)
Ow1	-0.1303(4)	0.4623(7)	0.4079(3)	0.8	0.966(9)
Ow2	0.1114(4)	0.4455(8)	0.4372(7)	0.74	5.29(4)

Table S4. Selected atomic bond distances for Zn-exchanged STS.

Atom1	**Atom 2**	**No**	**d(Å)**		**Atom1**	**Atom 2**	**No**	**d(Å)**
Ti1	O3	1x	1.860(4		K1	O2	1x	2.639(6)
	O6	1x	1.889(8)			Ow2	1x	2.72(8)
	O2	1x	1.95(1)			O8	1x	2.878(8)
	O4	1x	1.985(2)			O4	1x	2.904(8)
	O5	1x	2.045(6)			O6	1x	2.963(9)
	O1	1x	2.062(1)			O9	1x	3.066(4)
Si1	O7	1x	1.584(4)			O5	1x	3.367(7)
	O9	1x	1.596(9)			O7	1x	3.379(4)
	O2	1x	1.621(1)		Zn1/K2	Ow1	1x	1.711(4)
	O5	1x	1.650(6)			Ow2	1x	2.595(4)
Si2	O3	1x	1.509(2)			O5	1x	3.063(3)
	O8	1x	1.635(8)			O7	1x	3.100(8)
	O9	1x	1.663(9)			O6	1x	3.125(3)
	O1	1x	1.6824			O4	1x	3.17(9)
						O3	1x	3.203(4)
						Ow2	1x	3.344(6)
						O1	1x	3.380(9)
						O8	1x	3.385(1)

Table S5. Crystal data and Rietveld refinement parameters of Zn-CPT.

compound	Zn-CPT $(Na_{0.2}Ca_{0.4}K_{0.4}Mg_{0.2})Zn_{2.2}Al_6Si_{30}O_{72}\cdot 19H_2O$
formula weight	2646.68 g/mol
crystal system	monoclinic
space group (No.)	*C*2/m (12)
unit cell	a=17.648(9), b=17.963(1), c=7.405(7) Å, β=116.2(4)°
volume	2105.8(5) $Å^3$
D(calc)	2.0868(8) g/cm^3
No. reflections	1151
Reliability factors	R_p = 4.17, R_{wp} = 5.39, R_{exp} = 2.92, χ^2 = 1.83
structure factor	R_B = 1.53

Table S6. Atomic coordinates, occupancies and isotropic displacement parameters for Zn-exchanged CPT.

Atom	x	y	z	Occ.	*B* (Å^2)
Si1	0.17900(97)	0.1685(9)	0.0942(23)	0.8333	2.12(4)
Al1	0.17(9)	0.168(5)	0.0942(4)	0.1667	2.02(9)
Si2	0.21200(81)	0.41230(83)	0.5029(23)	0.8333	2.09(6)
Al2	0.21(2)	0.412(3)	0.502(9)	0.1667	1.80(3)
Si3	0.2084(11)	0.19115(74)	0.7145(20)	0.8333	1.61(8)
Al3	0.208(3)	0.1911(5)	0.714(50	0.1667	1.26(8)
Si4	0.06850(87)	0.29990(86)	0.4134(19)	0.8333	1.75(4)
Al4	0.068(5)	0.299(9)	0.413(4)	0.1667	1.60(9)
Si5	0	0.2190(12)	0	0.8333	2.3
Al5	0	0.21(9)	0	0.1667	2.3
O1	0.2009(16)	1/2	0.4617(45)		2.15(7)
O2	0.2320(13)	0.1225(12)	0.6109(37)		2.3
O3	0.1835(13)	0.156(1)	0.880(3)		0.8
O4	0.2307(12)	0.1026(12)	0.2459(31)		2.3
O5	0	0.3182(17)	1/2		2.3
O6	0.0817(13)	0.1677(11)	0.0505(31)		2.29(9)
O7	0.1230(11)	0.2304(12)	0.5442(31)		1.97(9)
O8	0.0123(13)	0.2733(13)	0.1829(26)		2.3
O9	0.2140(13)	0.2514(13)	0.1916(27)		2.3
O10	0.1155(13)	0.3768(12)	0.4198(32)		2.3
O11	0.2342(93)	1/2	0.035(28)	0.693305	2.3
O12	0.0384(39)	0	0.7182(87)	0.556151	2.3
O13	0.0765(14)	0.4376(13)	0.9411(30)	0.856389	2.3
O14	0	1/2	1/2	0.410834	2.3
O15	0	0.1203(50)	1/2	0.339063	1.79(7)
O16	0.0454(22)	0	0.1668(46)	0.72926	2.3
O17	0.1365(61)	0	0.723(12)	0.522007	1.08(9)
Zn1	0.0921(39)	0	0.464(10)	0.133	2.3
Zn2	0.0437(40)	1/2	0.270(21)	0.17	0.800(1)
Ca2	0.039(12)	1/2	0.21(8)	0.1	1.58(1)
K1	0.241(27)	1/2	0.049(82)	0.1	2.3
Mg1	0	0	1/2	0.1	0.8
Zn3	0	0	1/2	0.5	0.850(7)
Na1	0.143(46)	0	0.67(11)	0.05	2.3

Table S7. Selected atomic bond distances for Zn-exchanged CPT.

Si1|Al1	O6	1x	1.6007(292)	Zn1	O17	1x	1.7216(1057)
	O4	1x	1.6092(246)		Zn3|Mg1	1x	1.7597(798)
	O3	1x	1.6384(311)		O16	1x	1.9797(759)
	O9	1x	1.6509(271)		O12	1x	2.0921(809)
Si2|Al2	O1	1x	1.6001(156)		O12	1x	2.4536(1160)
	O10	1x	1.6611(255)		O15	2x	2.7868(860)
	O2	1x	1.6776(344)		O2	2x	3.1220(486)
Si3|Al3	O2	1x	1.6017(304)		O1	1x	3.4456(778)
	O3	1x	1.6032(312)	Zn2	O14	1x	2.1582(1555)
	O9	1x	1.6069(264)		O13	2x	2.2952(643)
	O7	1x	1.6366(217)		O1	1x	2.4959(665)
Si4|Al4	O10	1x	1.6012(274)		O10	2x	2.5477(449)
	O7	1x	1.6119(239)		O13	2x	2.9616(1490)
	O8	1x	1.6213(208)		Si2|Al2	2x	3.1223(555)
	O5	1x	1.6330(186)		Ca2	1x	3.1903(5586)
Si5|Al5	O8	2x	1.6041(251)	Ca2	O13	2x	2.1556(1645)
	O6	2x	1.6097(250)		O14	1x	2.5285(5907)
					O13	2x	2.6126(5335)
					O1	1x	2.6323(2135)
					O10	2x	2.6980(2174)
					Ca2	1x	2.7898(7513)
					Zn2	1x	3.1903(5586)
					Si2|Al2	2x	3.2638(2018)
				K1	O17	1x	2.0729(3979)
					Na1	1x	2.1804(7328)
					O13	2x	2.8761(4353)
					O3	2x	3.0471(1735)
					O4	2x	3.0627(5291)
					O2	2x	3.2174(4464)
					O1	1x	3.4285(6629)
					O12	1x	3.4921(4317)
				Zn3|Mg1	Zn1	2x	1.7597(798)
					O15	2x	2.1610(898)
					O17	2x	2.2389(840)
					Na1	2x	2.2682(7060)
					O16	2x	2.9119(416)
				Na1	O12	1x	2.0293(9330)
					K1	1x	2.1804(7328)
					Zn3|Mg1	1x	2.2682(7060)
					O11	1x	2.2984(6234)
					O2	2x	2.8476(5988)
					O3	2x	3.1303(3231)
					O15	2x	3.1328(5149)
					O12	1x	3.2211(6128)
					O1	1x	3.3042(9521)

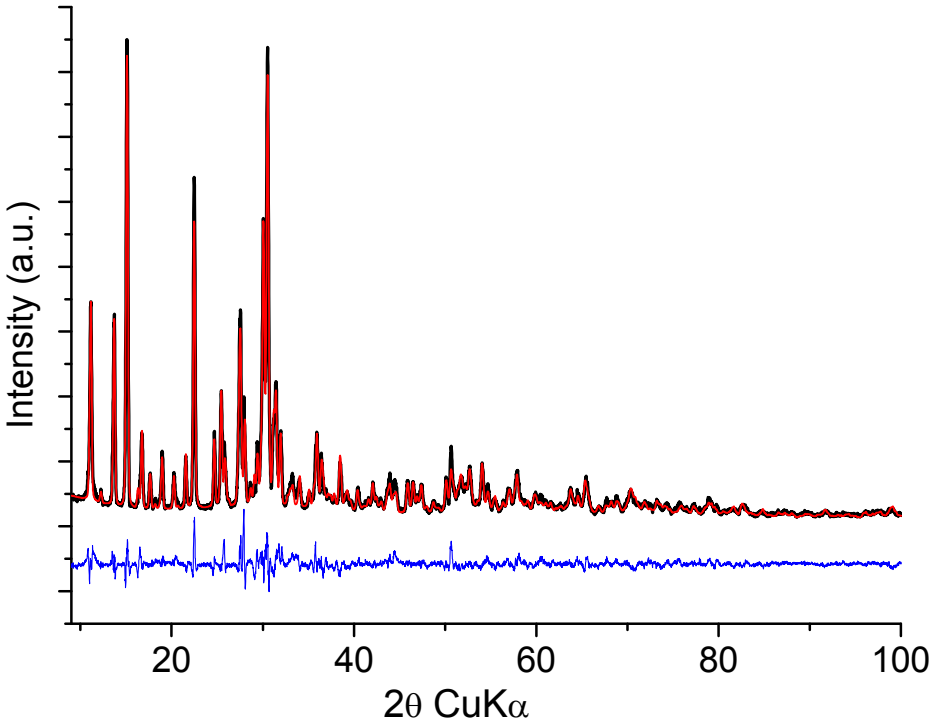

Figure S3. Experimental (black line) and simulated (red line) powder XRD patterns of Zn-STS.

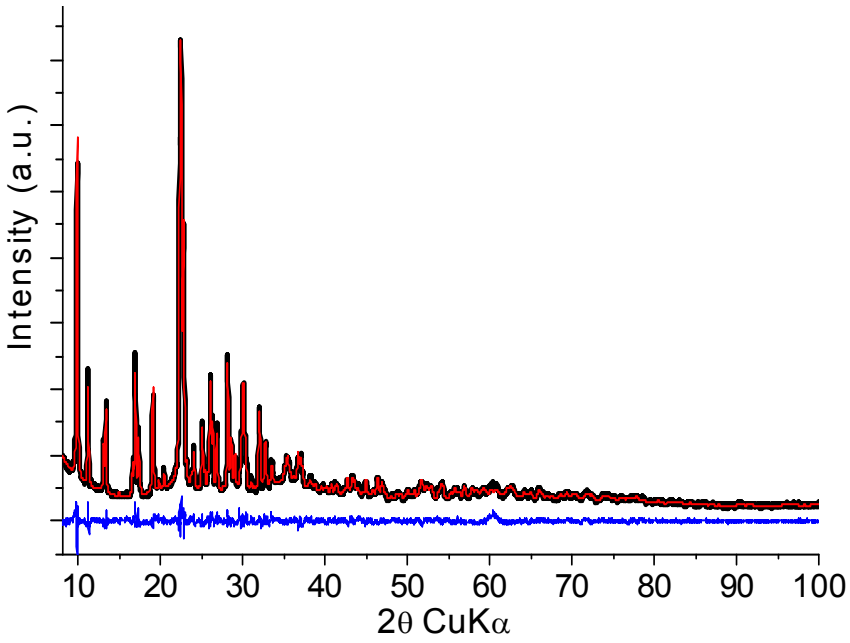

Figure S4. Experimental (black line) and simulated (red line) powder XRD patterns of Zn-CPT.

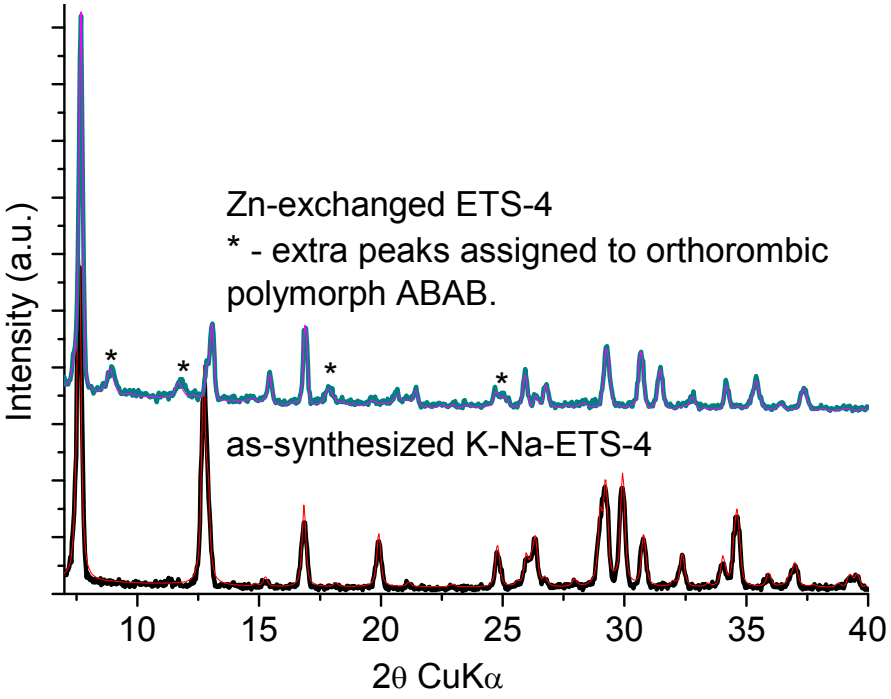

Figure S5. Le Bail fit of powder XRD patterns of the as-synthesized and Zn-exchanged ETS-4.

Single crystal X-ray diffraction. The single crystal X-ray diffraction analysis was performed on Zn-ETS-4. Crystal was mounted on a glass fiber and the diffraction data were collected at room temperature by ω-scan technique, on an Agilent Diffraction SuperNovaDual four-circle diffractometer equipped with Atlas CCD detector using mirror-monochromatized MoKα radiation from micro-focus source (λ = 0.7107 Å). The determination of cell parameters, data integration, scaling and absorption correction were carried out using the CrysAlis Pro program package[10]. The structures were solved by direct methods (SHELXS-97)[11] and refined by full-matrix least-square procedures on F2 (SHELXL-97)[11].

Details from the single crystal refinement are shown in Tables S8-S10.

Table S8. Single crystal data of Zn-ETS-4.

compound	Zn-ETS-4 $Zn_{3.15}H_{4.76}Si_{12}Ti_5O_{39}$ $6.6H_2O$
formula weight	1510.1(1) g/mol
wavelength (Å)	Mo Kα (0.71073)
T (K)	290(2)
crystal system	Orthorhombic
space group (No.)	*Cmmm* (65)
unit cell	a =22.879(6) Å, b=7.2161(15) Å, c=6.765(2) Å
volume	1116.8(5) $Å^3$
D(calc)	2.2450(4) g/cm^3
μ mm^{-1}	2.913
θ range	3.01^o – 26.05^o
index ranges	$-26 \leq h \leq 26$ $-8 \leq k \leq 8$ $-7 \leq l \leq 8$
collected reflections	604
No.indep. reflections	233
R1 *wR2 (all data)*	0.127 0.292

Table S9. Atomic coordinates, occupancies and isotropic displacement parameters for Zn-exchanged ETS-4.

Atom	x	y	z	Occ.	B (Å^2)
Zn1	1/4	1/4	0	0.43	4.50(1)
Zn2	0.1320(8)	0	0.600(3)	0.18	4.65(8)
Si1	0.3375(3)	0	0.2268(10)	1	3.07(9)
Si2	0.0654(6)	0.407(2)	1/2	0.5	4.34(3)
Ti1	1/4	1/4	1/2	1	4.10(6)
Ti2	0	0	1/2	0.5	4.73(7)
O1	0.164(3)	1/2	0	1	19.7(4)
O2	0.3051(6)	0.1783(18)	0.288(3)	1	7.89(6)
O3	0.4014(8)	0	0.303(4)	1	5.92(2)
O4	0	1/2	1/2	1	6.47(4)
O5	0.0637(18)	0.180(5)	1/2	0.5	7.34(3)
O6	0.2176(11)	0	1/2	1	4.73(7)
O7	0	0	0.787(14)	0.25	7.10(6)
O21	0.2030(17)	0	0	0.73	5.60(6)
O22	0	0.326(15)	0	0.64	16.5(8)
O23	0	0	0	0.57	7.10(6)

Table S10. Selected atomic bond distances for Zn-exchanged ETS-4.

Atom1	Atom2	No	d(Å)			Atom1	Atom2	d(Å)
Si1	O1	1x	1.535(7)		Zn1	O21	2x	2.100(2)
	O2	2x	1.542(2)			O2	4x	2.378(2)
	O3	1x	1.550(2)			O1	2x	2.669(5)
Si2	Si2	1x	1.342(2)		Zn2	O6	1x	2.072(3)
	O5	1x	1.638(4)			O5	2x	2.142(4)
	O4	1x	1.640(2)			O2	2x	2.834(2)
	O3	2x	1.674(3)					
Ti1	O6	2x	1.950(2)					
	O2	4x	1.978(2)					
Ti2	O7	2x	1.942(2)					
	O5	4x	1.952(4)					

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