Solution Equilibrium behind the Room-Temperature Synthesis of Nanocrystalline Titanium Dioxide

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Supplementary materials

Table TS1. Crystal data and structure refinement for $(NH_4)_2[Ti(C_3H_4O_3)_3](H_2O)_3$.

Identification code	tilac1_0m	
Empirical formula	$C_9H_{26}N_2O_{12}Ti$	
Formula weight	402.22	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Hexagonal	
Space group	P3	
Unit cell dimensions	a = 15.3040(15) Å	α= 90°.
	b = 15.3040(15) Å	β= 90°.
	c = 6.6658(13) Å	γ = 120°.
Volume	1352.0(3) $Å^3$	
Z	3	
Density (calculated)	1.482 Mg/m^3	
Absorption coefficient	0.535 mm^{-1}	
F(000)	636	
Crystal size	0.31 x 0.28 x 0.08 mm^3	
Theta range for data collection	2.66 to 23.82°.	
Index ranges	-17<=h<=17, -17<=k<=17, -7<=l<=7	
Reflections collected	9275	
Independent reflections	2772 [R(int) = 0.0449]	
Completeness to theta = 23.82°	99.7 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9585 and 0.8518	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2772 / 36 / 262
Goodness-of-fit on F^2	0.968
Final R indices [I>2sigma(I)]	R1 = 0.0219, wR2 = 0.0509
R indices (all data)	R1 = 0.0237, wR2 = 0.0516
Absolute structure parameter	-0.03(10)
Largest diff. peak and hole	0.120 and -0.127 e.$Å^{-3}$

Table TS2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $(NH_4)_2[Ti(C_3H_4O_3)_3](H_2O)_3$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ti(1)	3333	6667	8779(5)	26(1)
Ti(2)	0	10000	-1171(5)	26(1)
Ti(3)	6667	3333	6998(5)	24(1)
O(2)	-1002(7)	8939(7)	805(14)	32(2)
O(1)	4235(7)	7756(7)	6798(15)	38(2)
O(3)	6385(7)	2152(6)	8348(13)	33(2)
O(8)	-2027(8)	7286(7)	1248(15)	42(2)
C(1)	5464(10)	1341(11)	5400(20)	33(3)
O(7)	5006(9)	651(8)	4234(16)	60(3)
C(8)	5411(10)	8162(10)	9410(20)	32(3)
C(2)	5774(10)	1188(9)	7490(20)	32(3)
O(9)	5772(9)	9043(9)	6300(17)	59(3)
C(7)	5153(10)	8357(10)	7350(20)	33(3)
C(9)	6328(11)	8039(14)	9390(30)	53(4)
C(4)	-1459(9)	8021(10)	210(20)	28(3)
O(6)	5732(7)	2266(7)	5006(13)	35(2)
O(5)	-418(7)	8810(6)	-2594(13)	32(2)
O(4)	4552(6)	7288(7)	10186(13)	34(2)
O(10)	444(10)	8594(9)	-6084(18)	49(3)
O(11)	-3125(10)	7507(10)	4484(19)	57(3)
O(12)	6735(10)	10125(9)	2872(18)	51(3)
N(1)	3687(10)	8568(10)	3535(18)	44(3)
N(2)	4623(10)	2496(10)	1826(19)	36(3)
C(3)	4865(12)	525(12)	8770(20)	51(4)
C(6)	-1132(15)	7014(11)	-2380(30)	60(5)
C(5)	-1269(10)	7902(10)	-1980(20)	34(3)

Table TS3. Bond lengths [Å] and angles [°] for $(NH_4)_2[Ti(C_3H_4O_3)_3](H_2O)_3$.

Ti(1)-O(4)#1	1.868(9)
Ti(1)-O(4)	1.868(9)
Ti(1)-O(4)#2	1.868(9)
Ti(1)-O(1)#1	2.032(10)
Ti(1)-O(1)	2.032(10)
Ti(1)-O(1)#2	2.032(10)
Ti(2)-O(5)	1.860(9)
Ti(2)-O(5)#3	1.860(9)
Ti(2)-O(5)#4	1.860(9)
Ti(2)-O(2)#3	2.057(9)
Ti(2)-O(2)#4	2.057(9)
Ti(2)-O(2)	2.057(9)
Ti(3)-O(3)	1.866(8)
Ti(3)-O(3)#5	1.866(8)
Ti(3)-O(3)#6	1.866(8)
Ti(3)-O(6)#5	2.035(9)
Ti(3)-O(6)	2.035(9)
Ti(3)-O(6)#6	2.035(9)
O(2)-C(4)	1.280(16)
O(1)-C(7)	1.289(17)
O(3)-C(2)	1.414(15)
O(8)-C(4)	1.234(16)
C(1)-O(7)	1.215(17)
C(1)-O(6)	1.289(17)
C(1)-C(2)	1.523(19)
C(8)-O(4)	1.424(16)
C(8)-C(7)	1.50(2)
C(8)-C(9)	1.51(2)
C(8)-H(8A)	0.9800
C(2)-C(3)	1.51(2)
C(2)-H(2A)	0.9800
O(9)-C(7)	1.223(16)
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600
C(4)-C(5)	1.514(19)

O(5)-C(5)	1.410(16)
O(10)-H(10A)	0.79(13)
O(10)-H(10B)	0.84(10)
O(11)-H(11A)	0.86(11)
O(11)-H(11B)	0.87(11)
O(12)-H(12A)	0.88(11)
O(12)-H(12B)	0.86(11)
N(1)-H(1A)	1.1538
N(1)-H(1B)	0.8053
N(1)-H(1C)	0.9461
N(1)-H(1D)	1.1613
N(2)-H(2AA)	0.95(9)
N(2)-H(2BA)	0.96(10)
N(2)-H(2CA)	0.96(10)
N(2)-H(2DA)	0.97(10)
C(3)-H(3A)	0.9600
C(3)-H(3B)	0.9600
C(3)-H(3C)	0.9600
C(6)-C(5)	1.50(2)
C(6)-H(6A)	0.9600
C(6)-H(6B)	0.9600
C(6)-H(6C)	0.9600
C(5)-H(5A)	0.9800

O(4)#1-Ti(1)-O(4)	97.0(4)
O(4)#1-Ti(1)-O(4)#2	97.0(4)
O(4)-Ti(1)-O(4)#2	97.0(4)
O(4)#1-Ti(1)-O(1)#1	79.2(4)
O(4)-Ti(1)-O(1)#1	159.8(4)
O(4)#2-Ti(1)-O(1)#1	103.2(4)
O(4)#1-Ti(1)-O(1)	103.2(4)
O(4)-Ti(1)-O(1)	79.2(4)
O(4)#2-Ti(1)-O(1)	159.8(4)
O(1)#1-Ti(1)-O(1)	82.3(4)
O(4)#1-Ti(1)-O(1)#2	159.8(4)
O(4)-Ti(1)-O(1)#2	103.2(4)
O(4)#2-Ti(1)-O(1)#2	79.2(4)
O(1)#1-Ti(1)-O(1)#2	82.3(4)

O(1)-Ti(1)-O(1)#2	82.3(4)
O(5)-Ti(2)-O(5)#3	96.3(4)
O(5)-Ti(2)-O(5)#4	96.3(4)
O(5)#3-Ti(2)-O(5)#4	96.3(4)
O(5)-Ti(2)-O(2)#3	159.1(4)
O(5)#3-Ti(2)-O(2)#3	78.3(3)
O(5)#4-Ti(2)-O(2)#3	104.3(4)
O(5)-Ti(2)-O(2)#4	104.3(4)
O(5)#3-Ti(2)-O(2)#4	159.1(4)
O(5)#4-Ti(2)-O(2)#4	78.3(4)
O(2)#3-Ti(2)-O(2)#4	83.4(4)
O(5)-Ti(2)-O(2)	78.3(3)
O(5)#3-Ti(2)-O(2)	104.3(4)
O(5)#4-Ti(2)-O(2)	159.1(4)
O(2)#3-Ti(2)-O(2)	83.4(4)
O(2)#4-Ti(2)-O(2)	83.4(4)
O(3)-Ti(3)-O(3)#5	98.7(4)
O(3)-Ti(3)-O(3)#6	98.7(4)
O(3)#5-Ti(3)-O(3)#6	98.7(4)
O(3)-Ti(3)-O(6)#5	101.3(4)
O(3)#5-Ti(3)-O(6)#5	78.9(4)
O(3)#6-Ti(3)-O(6)#5	159.9(4)
O(3)-Ti(3)-O(6)	78.9(4)
O(3)#5-Ti(3)-O(6)	159.9(4)
O(3)#6-Ti(3)-O(6)	101.3(4)
O(6)#5-Ti(3)-O(6)	82.0(4)
O(3)-Ti(3)-O(6)#6	159.9(4)
O(3)#5-Ti(3)-O(6)#6	101.3(4)
O(3)#6-Ti(3)-O(6)#6	78.9(4)
O(6)#5-Ti(3)-O(6)#6	82.0(4)
O(6)-Ti(3)-O(6)#6	82.0(4)
C(4)-O(2)-Ti(2)	116.8(8)
C(7)-O(1)-Ti(1)	116.8(9)
C(2)-O(3)-Ti(3)	121.8(8)
O(7)-C(1)-O(6)	123.5(13)
O(7)-C(1)-C(2)	122.7(13)
O(6)-C(1)-C(2)	113.8(11)
O(4)-C(8)-C(7)	107.9(10)

O(4)-C(8)-C(9)	111.5(11)
C(7)-C(8)-C(9)	111.8(12)
O(4)-C(8)-H(8A)	108.5
C(7)-C(8)-H(8A)	108.5
C(9)-C(8)-H(8A)	108.5
O(3)-C(2)-C(3)	112.2(11)
O(3)-C(2)-C(1)	107.7(10)
C(3)-C(2)-C(1)	111.4(12)
O(3)-C(2)-H(2A)	108.5
C(3)-C(2)-H(2A)	108.5
C(1)-C(2)-H(2A)	108.5
O(9)-C(7)-O(1)	123.3(13)
O(9)-C(7)-C(8)	121.8(13)
O(1)-C(7)-C(8)	114.9(11)
C(8)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(8)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
O(8)-C(4)-O(2)	125.1(12)
O(8)-C(4)-C(5)	121.4(12)
O(2)-C(4)-C(5)	113.5(11)
C(1)-O(6)-Ti(3)	117.2(8)
C(5)-O(5)-Ti(2)	120.8(8)
C(8)-O(4)-Ti(1)	121.0(8)
H(10A)-O(10)-H(10B)	106(10)
H(11A)-O(11)-H(11B)	105(10)
H(12A)-O(12)-H(12B)	104(10)
H(1A)-N(1)-H(1B)	107.1
H(1A)-N(1)-H(1C)	104.3
H(1B)-N(1)-H(1C)	113.4
H(1A)-N(1)-H(1D)	113.1
H(1B)-N(1)-H(1D)	116.5
H(1C)-N(1)-H(1D)	101.8
H(2AA)-N(2)-H(2BA)	104(10)
H(2AA)-N(2)-H(2CA)	117(10)
H(2BA)-N(2)-H(2CA)	110(10)

H(2AA)-N(2)-H(2DA)	107(10)
H(2BA)-N(2)-H(2DA)	102(10)
H(2CA)-N(2)-H(2DA)	115(10)
C(2)-C(3)-H(3A)	109.5
C(2)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	109.5
C(2)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
C(5)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
O(5)-C(5)-C(6)	111.2(11)
O(5)-C(5)-C(4)	107.5(11)
C(6)-C(5)-C(4)	113.8(12)
O(5)-C(5)-H(5A)	108.1
C(6)-C(5)-H(5A)	108.1
C(4)-C(5)-H(5A)	108.1

Symmetry transformations used to generate equivalent atoms:

#1 -y+1,x-y+1,z #2 -x+y,-x+1,z #3 -x+y-1,-x+1,z

#4 -y+1,x-y+2,z #5 -y+1,x-y,z #6 -x+y+1,-x+1,z

Table TS4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $(NH_4)_2[Ti(C_3H_4O_3)_3](H_2O)_3$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ti(1)	27(1)	27(1)	23(2)	0	0	14(1)
Ti(2)	26(1)	26(1)	24(2)	0	0	13(1)
Ti(3)	25(1)	25(1)	22(2)	0	0	13(1)
O(2)	34(5)	29(5)	30(5)	0(4)	6(4)	14(4)
O(1)	37(6)	38(6)	31(5)	11(5)	-2(4)	12(5)
O(3)	41(6)	29(5)	28(5)	0(4)	-8(4)	17(4)
O(8)	44(6)	32(6)	45(6)	7(5)	15(5)	16(5)
C(1)	27(7)	30(8)	36(8)	-2(6)	-4(6)	10(6)
O(7)	73(8)	39(6)	51(7)	-13(6)	-22(6)	15(6)
C(8)	26(7)	29(7)	34(8)	1(6)	-2(6)	9(6)
C(2)	34(8)	23(7)	39(8)	-1(6)	-3(6)	14(6)
O(9)	48(7)	50(7)	62(7)	28(6)	9(6)	11(6)
C(7)	33(8)	26(7)	41(8)	5(6)	3(7)	14(7)
C(9)	32(9)	63(11)	62(11)	19(9)	2(7)	23(8)
C(4)	24(7)	28(8)	35(8)	1(6)	2(6)	14(6)
O(6)	37(5)	31(5)	31(5)	-1(4)	-12(4)	12(4)
O(5)	35(5)	28(5)	31(5)	0(4)	7(4)	14(4)
O(4)	29(5)	39(5)	29(5)	7(4)	-2(4)	13(4)
O(10)	67(8)	51(7)	38(7)	13(6)	14(6)	35(6)
O(11)	57(8)	63(9)	48(7)	-4(6)	1(6)	28(7)
O(12)	59(8)	52(7)	45(7)	9(6)	4(6)	29(6)
N(1)	60(8)	39(7)	38(7)	-2(6)	-13(6)	28(7)
N(2)	33(7)	43(8)	29(7)	4(6)	-1(6)	17(6)
C(3)	53(10)	40(9)	48(9)	3(7)	8(8)	14(8)
C(6)	78(12)	32(9)	62(11)	2(8)	36(10)	21(9)
C(5)	32(8)	30(7)	34(7)	-1(6)	1(6)	11(6)

Table TS5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $(NH_4)_2[Ti(C_3H_4O_3)_3](H_2O)_3$.

	x	y	z	U(eq)
H(8A)	5552	8738	10270	39
H(2A)	6179	859	7345	39
H(9A)	6475	7923	10733	79
H(9B)	6894	8640	8868	79
H(9C)	6200	7475	8560	79
H(1A)	3410(20)	8160(30)	2010(100)	90(70)
H(1B)	3722(11)	8180(30)	4290(50)	70(60)
H(1C)	3190(30)	8736(14)	3920(30)	80(70)
H(1D)	4400(50)	9360(50)	3400(20)	100(70)
H(3A)	5084	440	10064	76
H(3B)	4476	-121	8134	76
H(3C)	4457	836	8912	76
H(6A)	-1023	6979	-3787	90
H(6B)	-1725	6406	-1965	90
H(6C)	-559	7089	-1641	90
H(5A)	-1852	7813	-2754	41
H(2AA)	4990(100)	2830(100)	650(180)	40(40)
H(2BA)	4290(120)	2860(120)	2200(300)	70(60)
H(11A)	-2800(160)	8150(90)	4600(300)	90(80)
H(2CA)	5010(120)	2470(140)	2900(200)	70(60)
H(2DA)	4070(110)	1850(90)	1400(300)	70(60)
H(10A)	500(150)	8970(130)	-7000(300)	80(70)
H(12A)	7240(110)	10020(140)	3100(300)	70(60)
H(10B)	190(130)	8740(130)	-5100(200)	60(60)
H(11B)	-2820(140)	7370(160)	3500(200)	80(70)
H(12B)	6330(140)	9800(140)	3800(200)	70(70)

Table TS6. Hydrogen bonds with H..A < r(A) + 2.000 Angstroms and <DHA > 110 deg.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N1-H1A	1.154	1.745	162.39	2.866	O4 [-y+1, x-y+1, z-1]
N1-H1B	0.805	2.081	155.10	2.832	O1
N1-H1C	0.946	1.806	165.86	2.733	O11 [-y+1, x-y+2, z]
N1-H1D	1.161	1.802	144.75	2.831	O7 [x, y+1, z]
N2-H2AA	0.949	1.947	175.94	2.895	O3 [-x+y+1, -x+1, z-1]
N2-H2BA	0.960	1.823	166.64	2.767	O12 [-x+y, -x+1, z]
O11-H11A	0.856	1.953	158.75	2.769	O10 [-x+y-1, -x+1, z+1]
N2-H2CA	0.958	1.892	173.40	2.846	O6
N2-H2DA	0.966	1.946	160.44	2.874	O8 [-y+1, x-y+1, z]
O10-H10A	0.785	2.081	164.80	2.846	O2 [-y+1, x-y+2, z-1]
O12-H12A	0.877	1.935	166.68	2.796	O10 [-x+y, -x+1, z+1]
O10-H10B	0.840	1.949	167.53	2.774	O5
O11-H11B	0.873	1.991	171.08	2.856	O8
O12-H12B	0.860	1.944	161.61	2.774	O9

Figure FS1 Packing of the molecules in the structure of $(NH_4)_2[Ti(C_3H_4O_3)_3](H_2O)_3$.

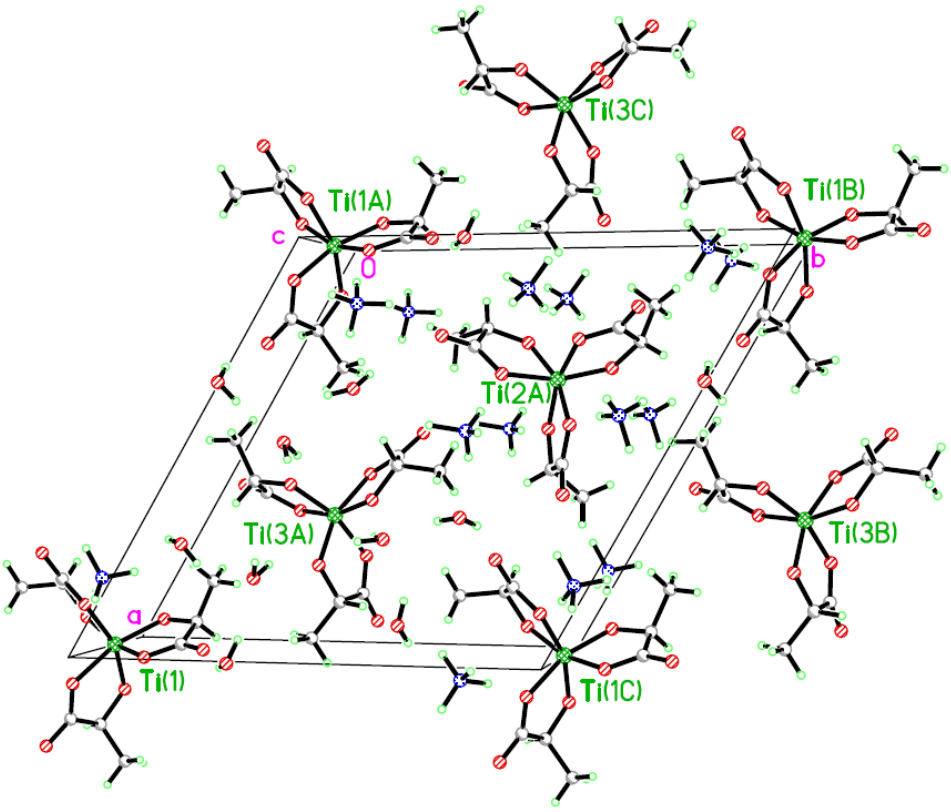


Figure FS2 High resolution TEM image of a dried methanol sample – example 1

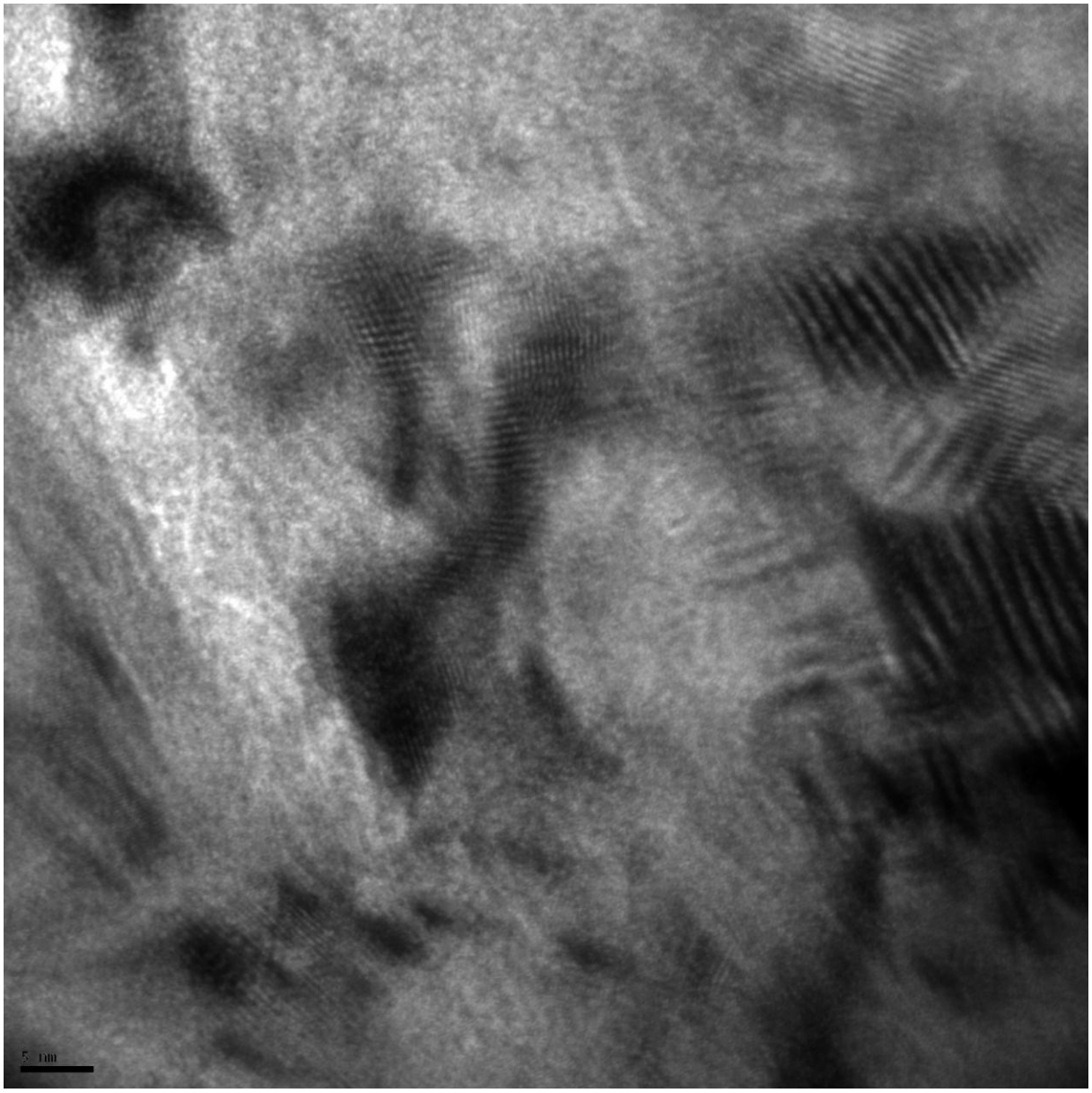


Figure FS3 High resolution TEM image of a dried methanol sample – example 2

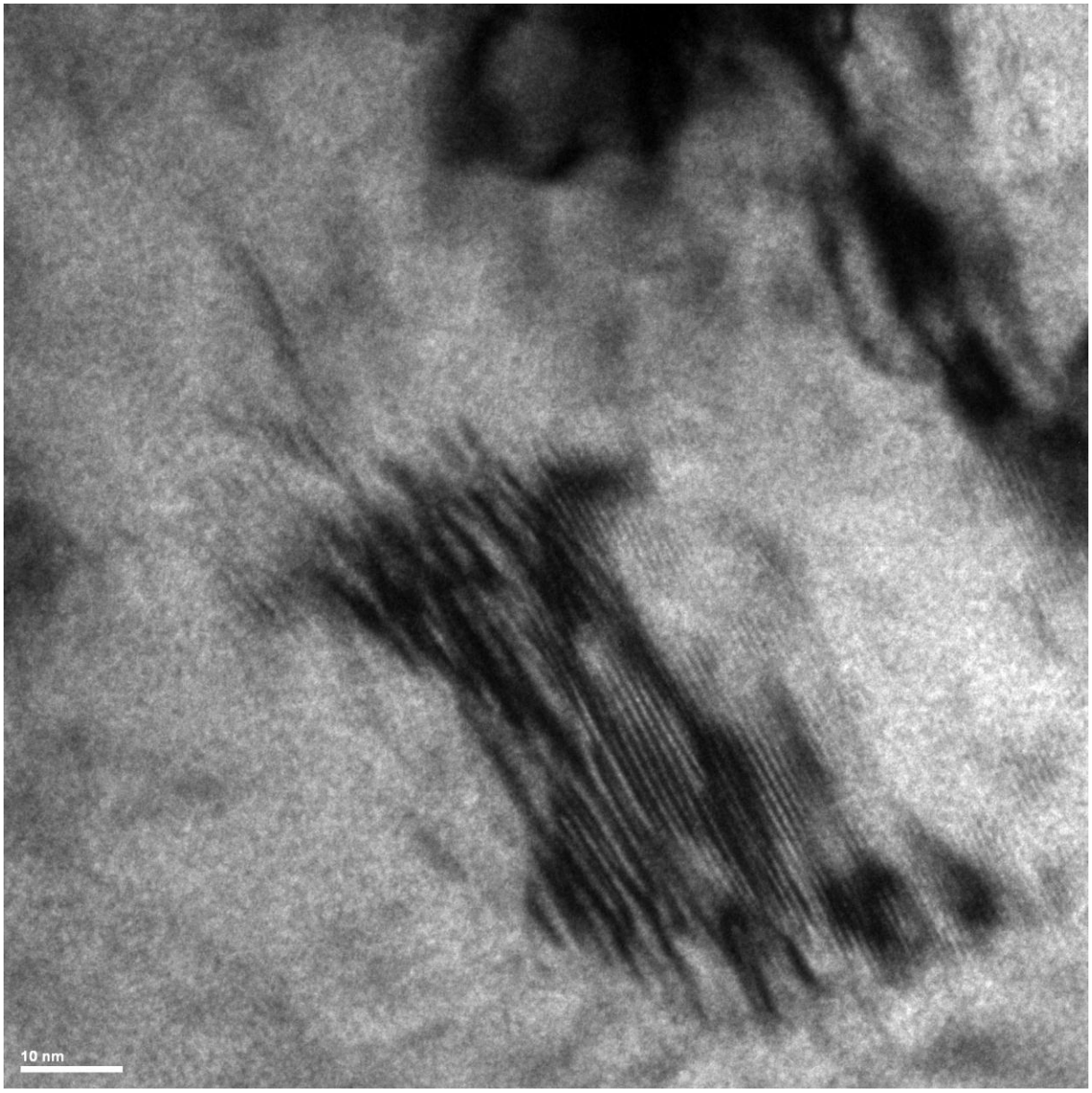
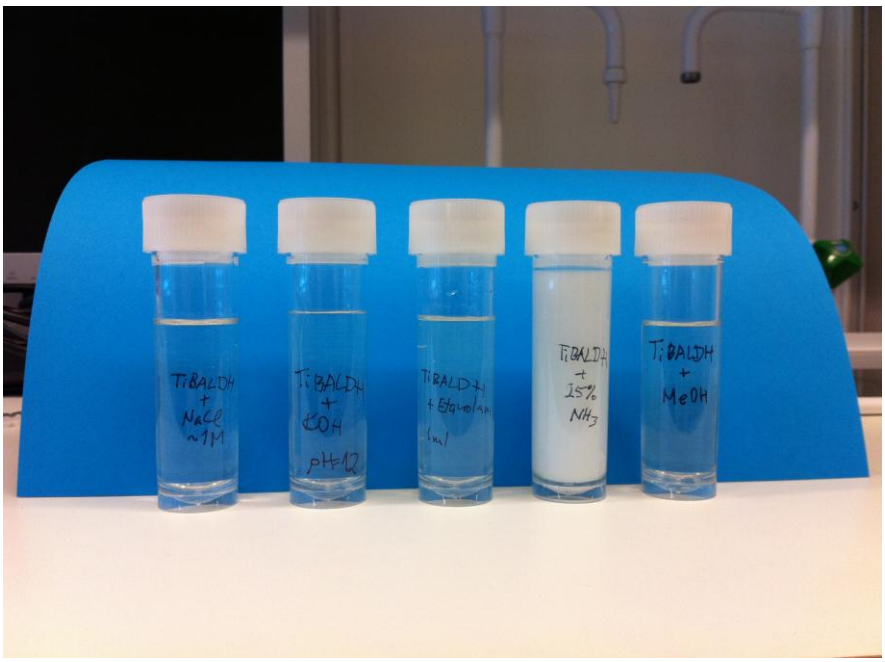


Figure FS4 Development of gelation in TiBALDH solutions with different agents

2h 

5h 

24h 

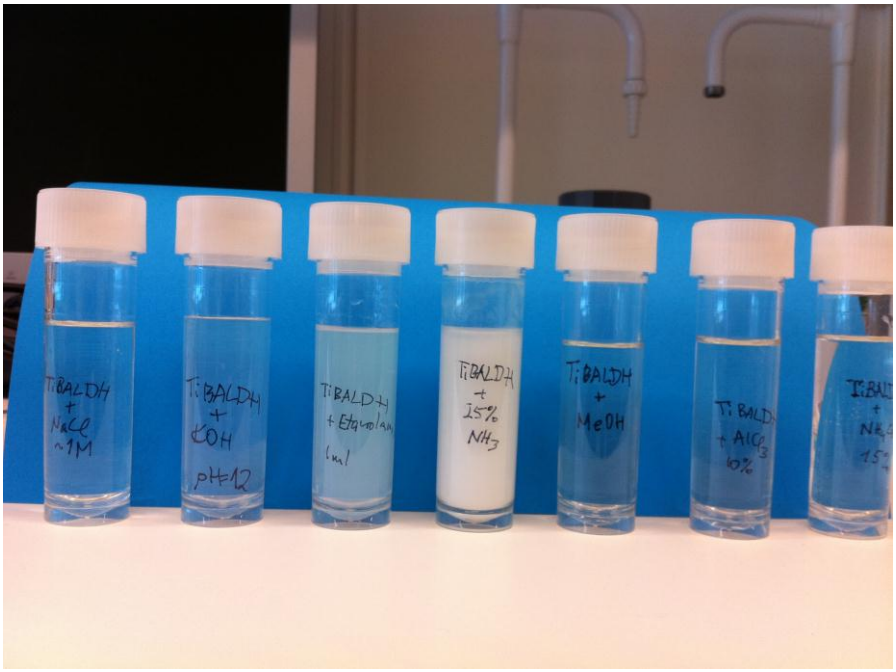
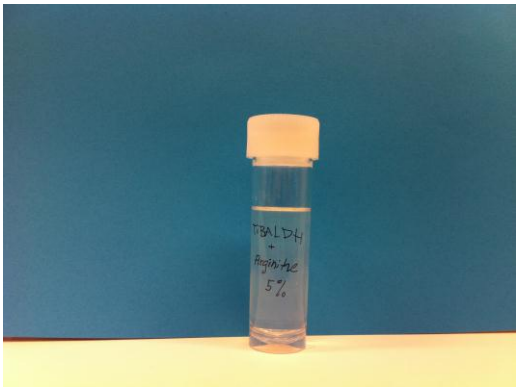
36h 

Figure FS5 Development of precipitation in TiBALDH solutions in the presence of Arginine

1h

3h

8h



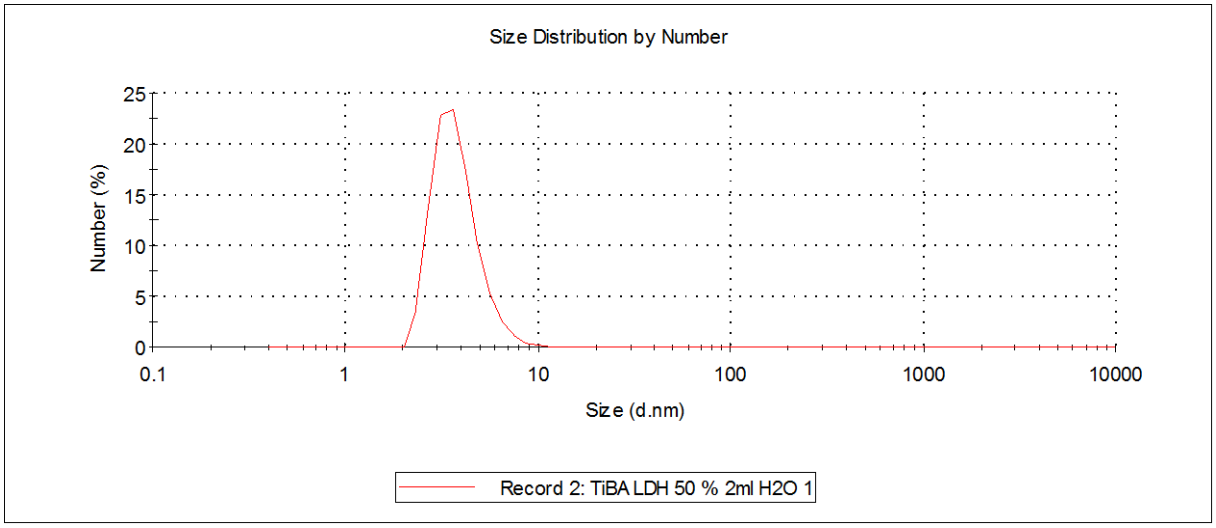
24h

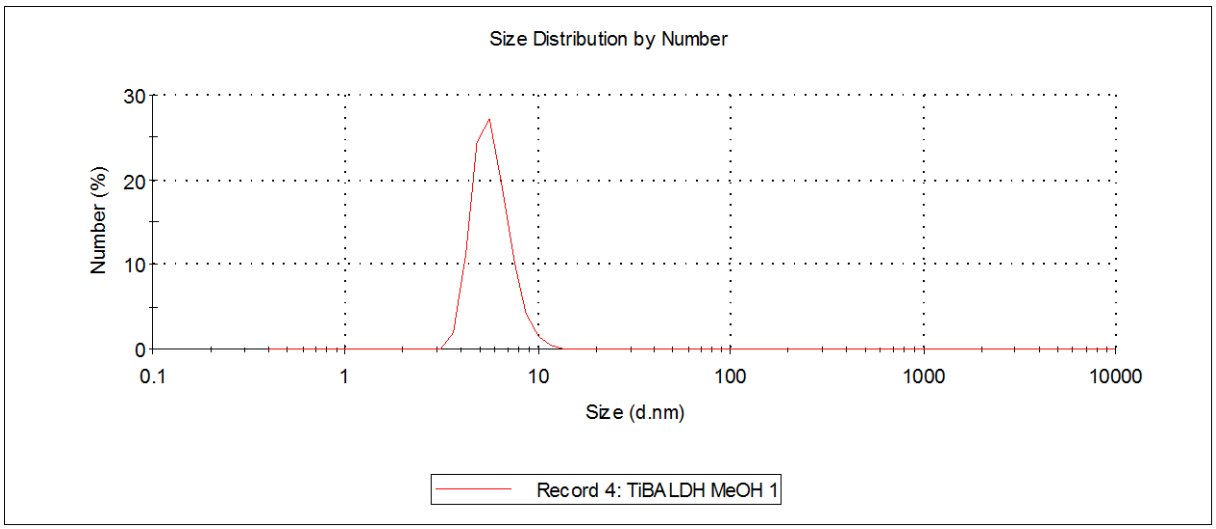
Table TS7 Average size and zeta-potential of colloids obtained from TiBALDH by dilution in different media

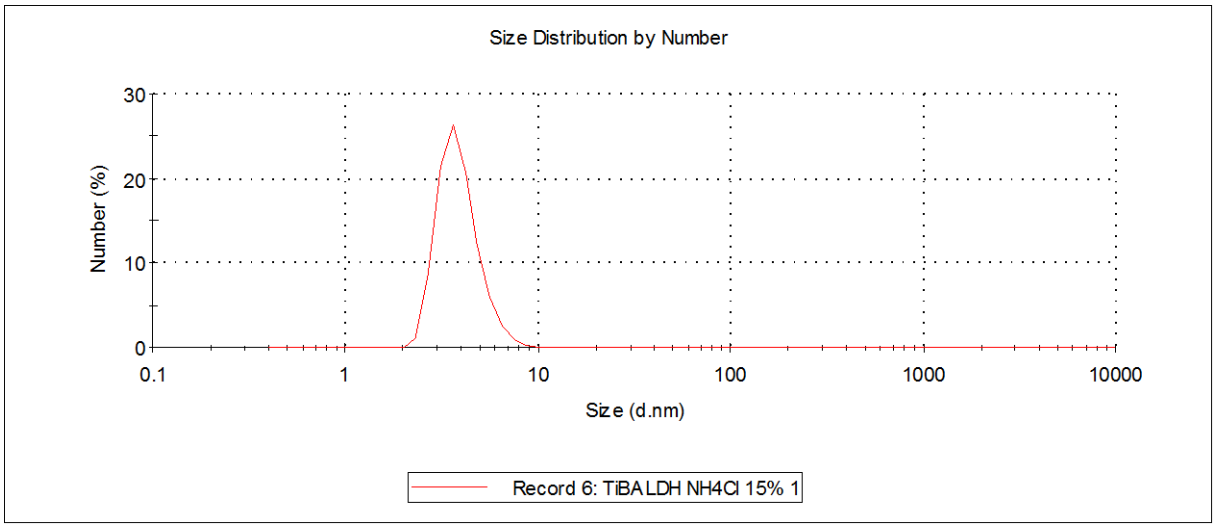
Sample	Size (nm)	width (nm)	size2	width2	size3	width3	Zeta potential (mV)	pH
H_2O 50%	3,8	1,075					-8,2	6.8
MeOH	5,8	1,35					-4,51	neutral
1M NH_4Cl	3,94	1,01					-0,472	4.6
1 M $AlCl_3$	4.0	1,06					-5,46	2.5
1M NaCl	6,1	1,53					-0,86	7.0
0.01 M KOH	1468	477	128,5	22			-37,5	12.0
5% Ethanolamine	4168	1000	647,4	212	142,1	40	-30	11.7

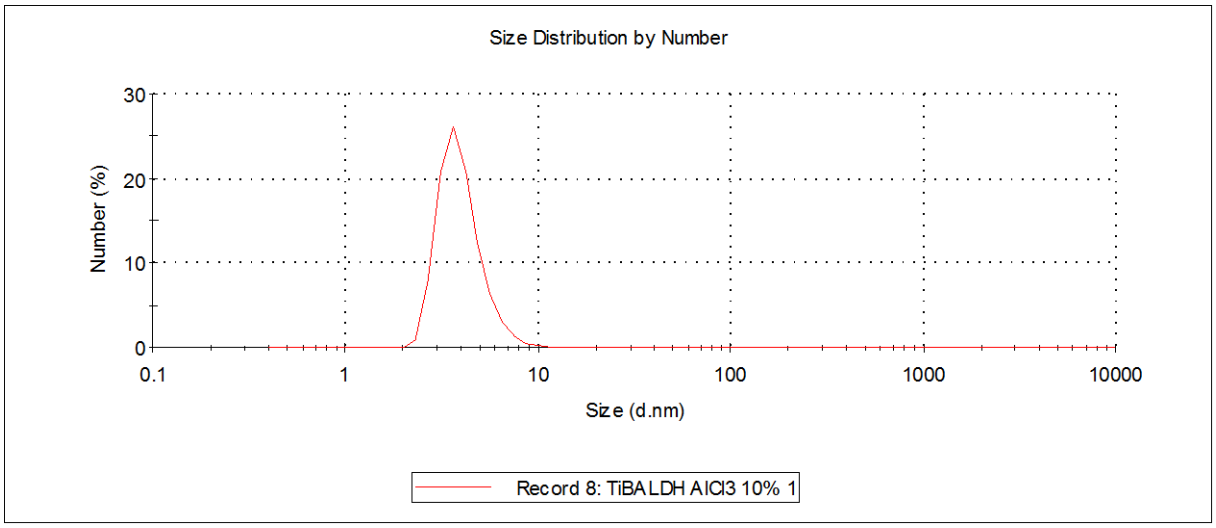
Relatively low values of zeta-potential in these cases might be caused by charge compensation in the inner sphere of the nanoparticles. Their solubility is then due to the hydrogen bonding to the solvent.
pH in 25% NH_3 solution was 12.3, in 5% Arginine 11.2

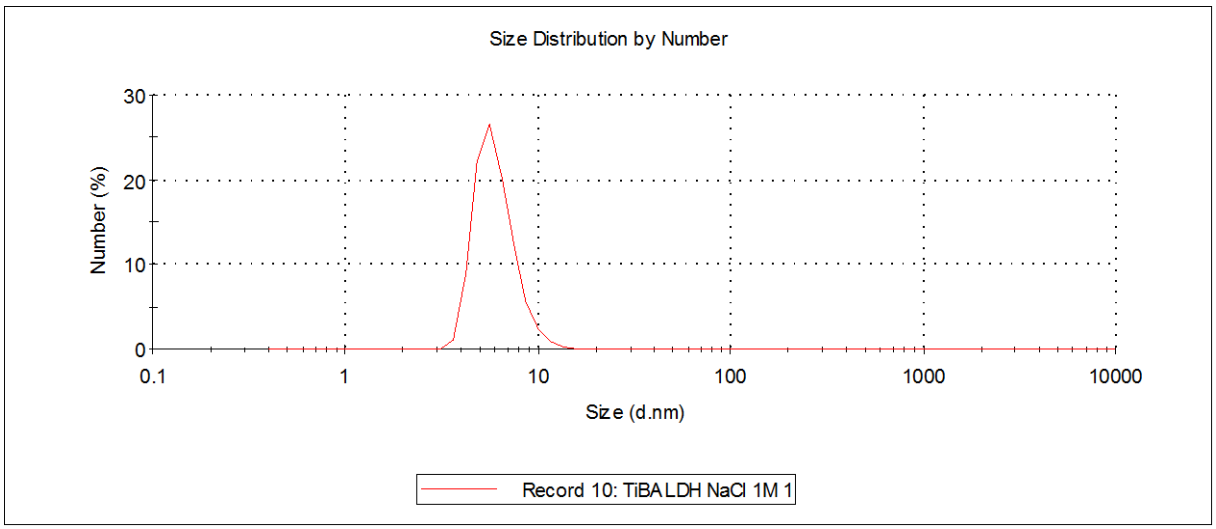
Figure FS6 Size distributions for colloids presented in Fig FS FS4

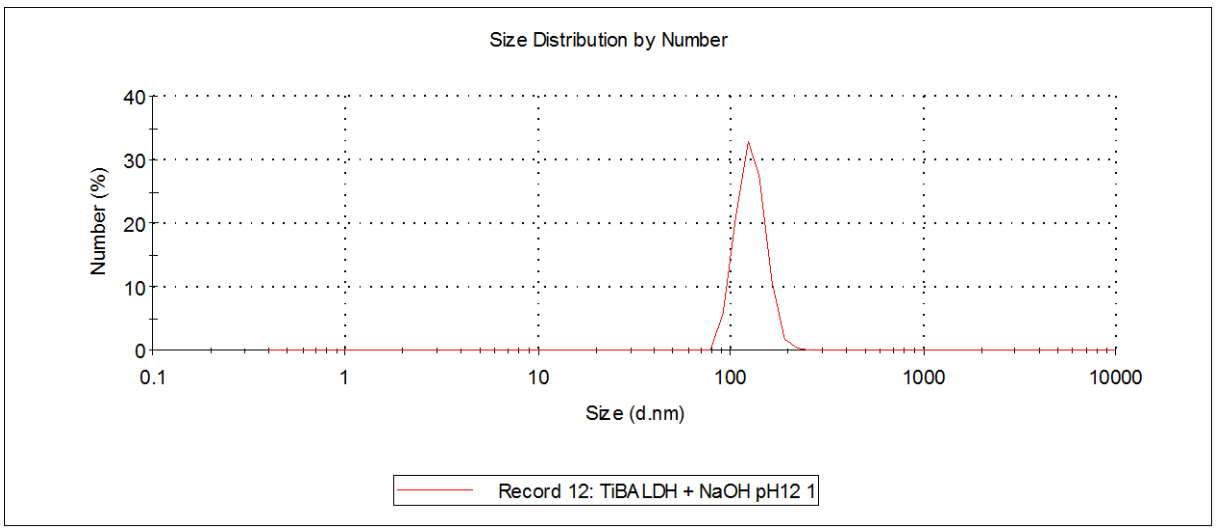


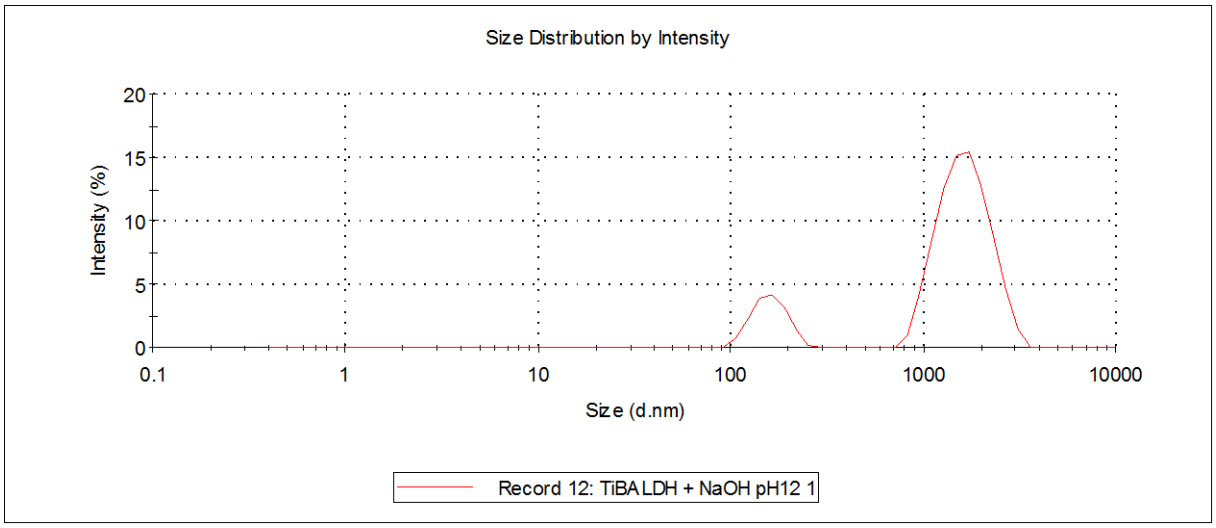


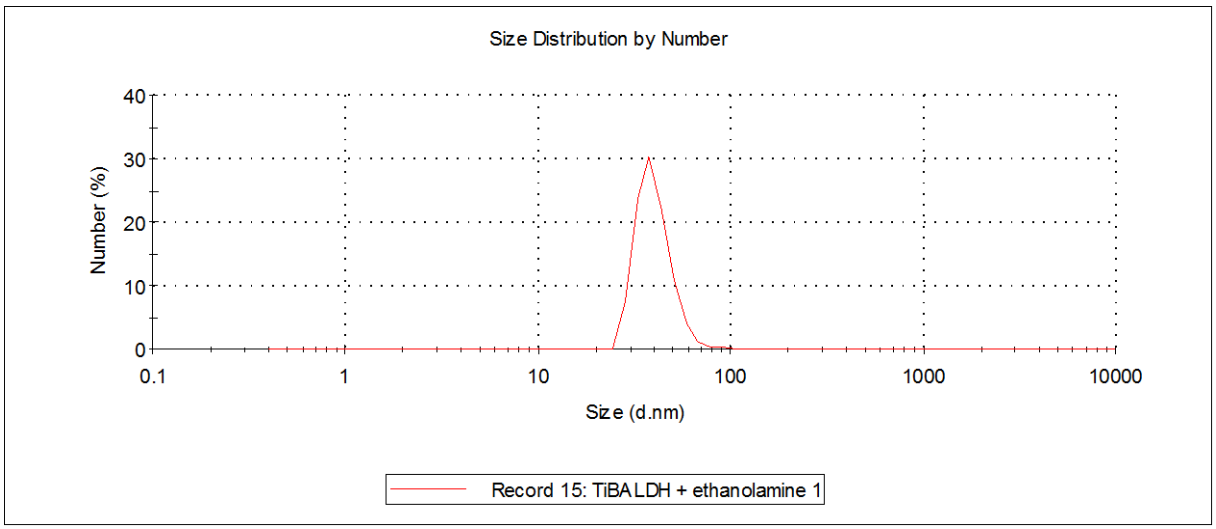












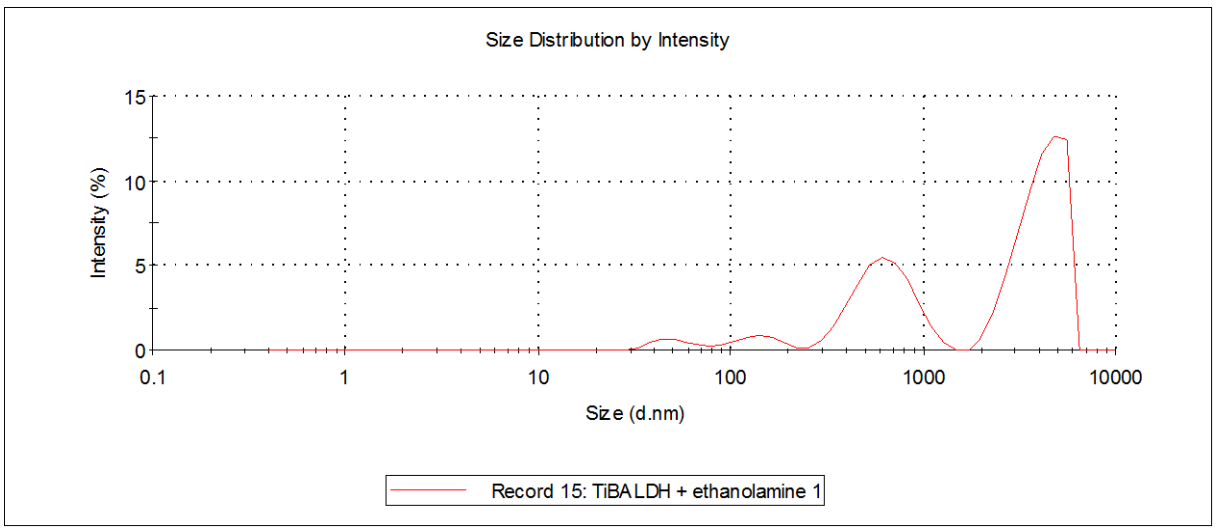


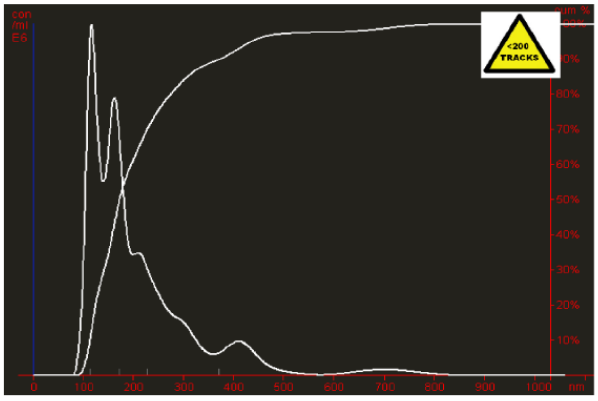
Figure FS7 Nanosight data on the size distribution in the colloid solution produced by addition of ethanol

NANOSIGHT

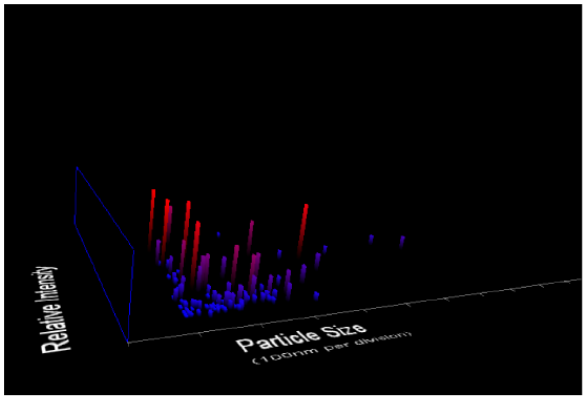
SAMPLE REPORT

Nanoparticle Tracking Analysis (NTA) Version 2.1 Build 0327

Sample: TiBALDH - Low camera setting
Video File: TiBALDH.avi; Analysis no. 003
Date/Time of Capture: 15 May 2009 09:27
Operator:
Comments:



Particle Size / Concentration



Particle Size / Relative Intensity 3D plot

Bin Centre (nm)	Concentration E6 particles / ml	Percentile Undersize
10	0.000	0.00%
30	0.000	0.00%
50	0.000	0.00%
70	0.000	0.00%
90	0.767	0.22%
110	6.971	6.91%
130	6.998	23.34%
150	6.172	34.23%
170	6.828	48.08%
190	3.912	57.89%
210	3.333	64.39%
230	2.906	70.51%
250	2.286	75.40%
270	1.814	79.26%
290	1.575	82.45%
310	1.311	85.25%
330	0.901	87.34%
350	0.634	88.73%
370	0.624	89.88%
390	0.800	91.24%
410	0.924	92.96%
430	0.803	94.67%
450	0.527	95.93%
470	0.290	96.67%
490	0.162	97.07%
510	0.101	97.30%

Bin Centre (nm)	Concentration E6 particles / ml	Percentile Undersize
530	0.063	97.46%
550	0.035	97.55%
570	0.022	97.60%
590	0.027	97.64%
610	0.048	97.71%
630	0.081	97.84%
650	0.116	98.03%
670	0.145	98.28%
690	0.162	98.58%
710	0.162	98.90%
730	0.148	99.20%
750	0.122	99.46%
770	0.091	99.66%
790	0.062	99.80%
810	0.038	99.90%
830	0.021	99.95%
850	0.011	99.98%
870	0.005	99.99%
890	0.002	100.00%
910	0.001	100.00%
930	0.000	100.00%
950	0.000	100.00%
970	0.000	100.00%
990	0.000	100.00%
1000-2000	0.000	100.00%

Results

Mean: 213 nm
Mode:117 nm
SD: 118 nm
D10: 113 nm
D50: 172 nm
D90: 372 nm
User Lines: 0, 0 nm
Concentration: 0.52 x 10^8 particles/ml

Measurement Conditions

Temperature: 22.00 ℃
Viscosity: 1.10 cP
Frames Per Second: 36.27
Measurement Time: 60 of 60 seconds
Drift Velocity: 3549 nm/s

Analysis Conditions

Brightness: -0
Gain: 1.00
Blur: 5x5
Detection Threshold: Auto
Max Blob Size (pixel area): 3000
Min Track Length: Auto
Min Expected Size: 100 nm

Figure FS8 The DLS results for the freshly prepared sample of clear solution produced by dilution of ethanol-precipitated TiBALDH with excess of water

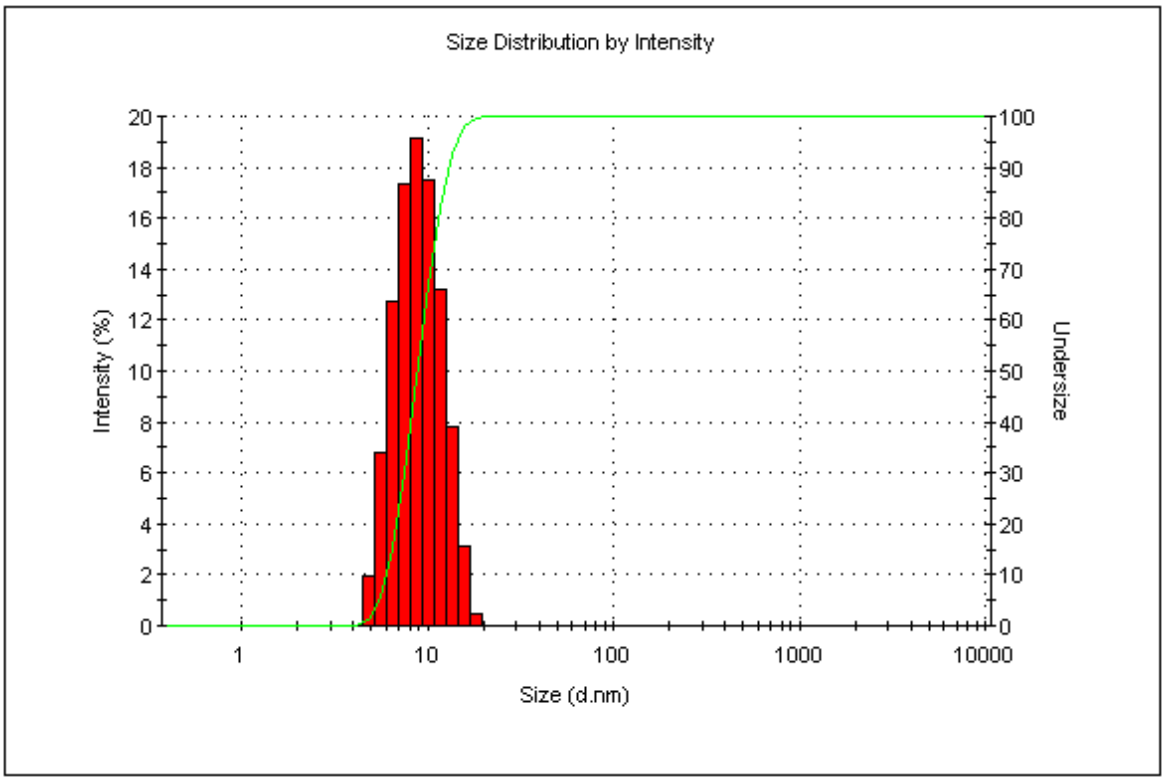
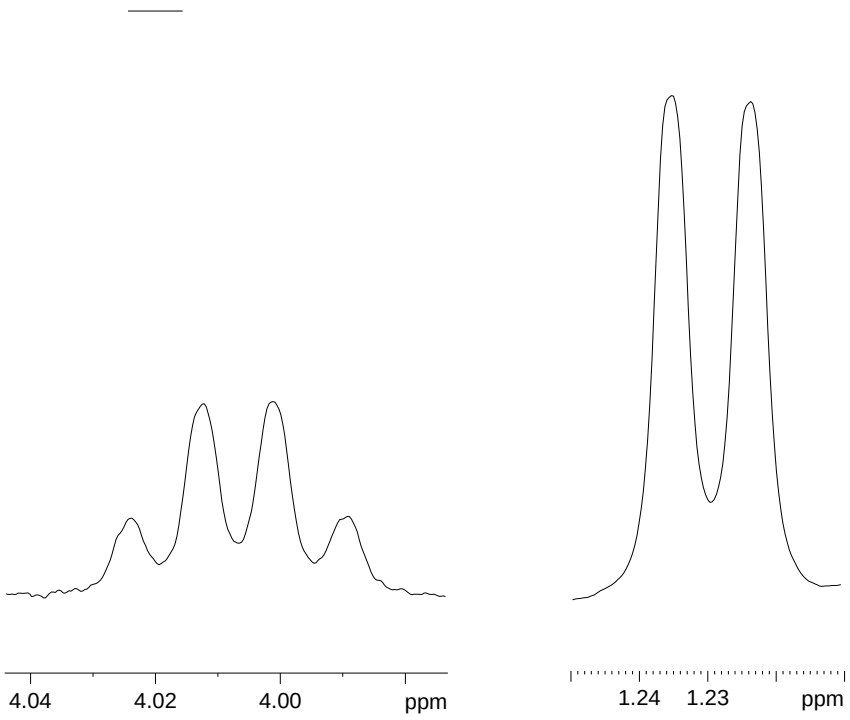
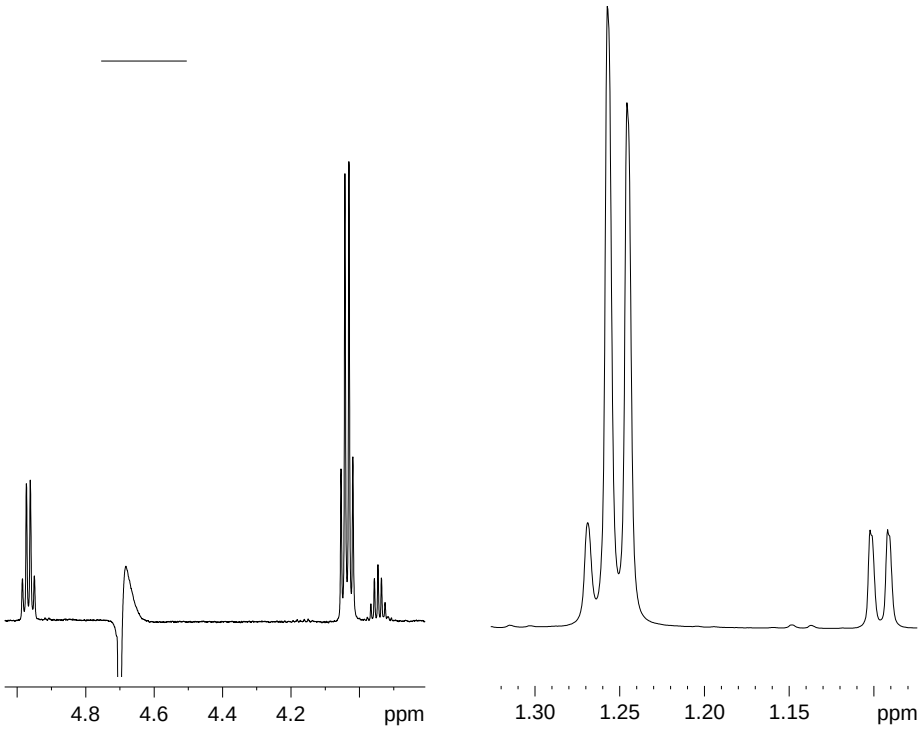


Figure FS9. The 1H NMR spectrum of nano-TiO2 produced from TiBALDH.




```
Current Data Parameters
NAME                  Ti
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20121023
Time               20.21
INSTRUM            spect
PROBHD   5 mm CPQCI 1H-
PULPROG     noesygppr1d
TD                 65536
SOLVENT          H2O+D2O
NS                    32
DS                     4
SWH            12345.679 Hz
FIDRES          0.188380 Hz
AQ              2.6542079 sec
RG                  1.01
DW                 40.500 usec
DE                 23.47 usec
TE                 300.0 K
D1            4.00000000 sec
D8            0.01000000 sec
D12           0.00002000 sec
D16           0.00020000 sec
TD0                    1
ZGOPTNS       -DFLAG_BLK

======== CHANNEL f1 ========
SFO1          600.1828208 MHz
NUC1                  1H
P0                 7.12 usec
P1                 7.12 usec
PLW1          9.19999981 W
PLW9          0.00001867 W

====== GRADIENT CHANNEL =====
GPNAM[1]      SMSQ10.100
GPNAM[2]      SMSQ10.100
GPZ1               50.00 %
GPZ2              -10.00 %
P16              1000.00 usec

F2 - Processing parameters
SI                 65536
SF            600.1800000 MHz
WDW                   EM
SSB       0
LB                 0.50 Hz
GB        0
PC                 1.00
```

Figure FS10. 1H NMR spectrum of TiBALDH diluted 80 times.




```
Current Data Parameters
NAME                  TiBal2
EXPNO                     11
PROCNO                     1

F2 - Acquisition Parameters
Date_              20121023
Time                  18.34
INSTRUM               spect
PROBHD   5 mm CPQCI 1H-
PULPROG      noesygppr1d
TD                    65536
SOLVENT           H2O+D2O
NS                       32
DS                        4
SWH              12345.679 Hz
FIDRES            0.188380 Hz
AQ                2.6542079 sec
RG                     1.01
DW                   40.500 usec
DE                   23.15 usec
TE                   300.0 K
D1               4.00000000 sec
D8               0.01000000 sec
D12              0.00002000 sec
D16              0.00020000 sec
TD0                       1
ZGOPTNS       -DFLAG_BLK

======== CHANNEL f1 ========
SFO1           600.1828208 MHz
NUC1                   1H
P0                   7.62 usec
P1                   7.62 usec
PLW1            9.19999981 W
PLW9            0.00002138 W

====== GRADIENT CHANNEL =====
GPNAM[1]       SMSQ10.100
GPNAM[2]       SMSQ10.100
GPZ1                50.00 %
GPZ2               -10.00 %
P16               1000.00 usec

F2 - Processing parameters
SI                    65536
SF               600.1800000 MHz
WDW                      EM
SSB       0
LB                    0.50 Hz
GB        0
PC                    1.00
```

Fig FS11 NOESY spectrum of TiBALDH in the lactate C*H*-region (water signal in the text of the paper is omitted for clarity)

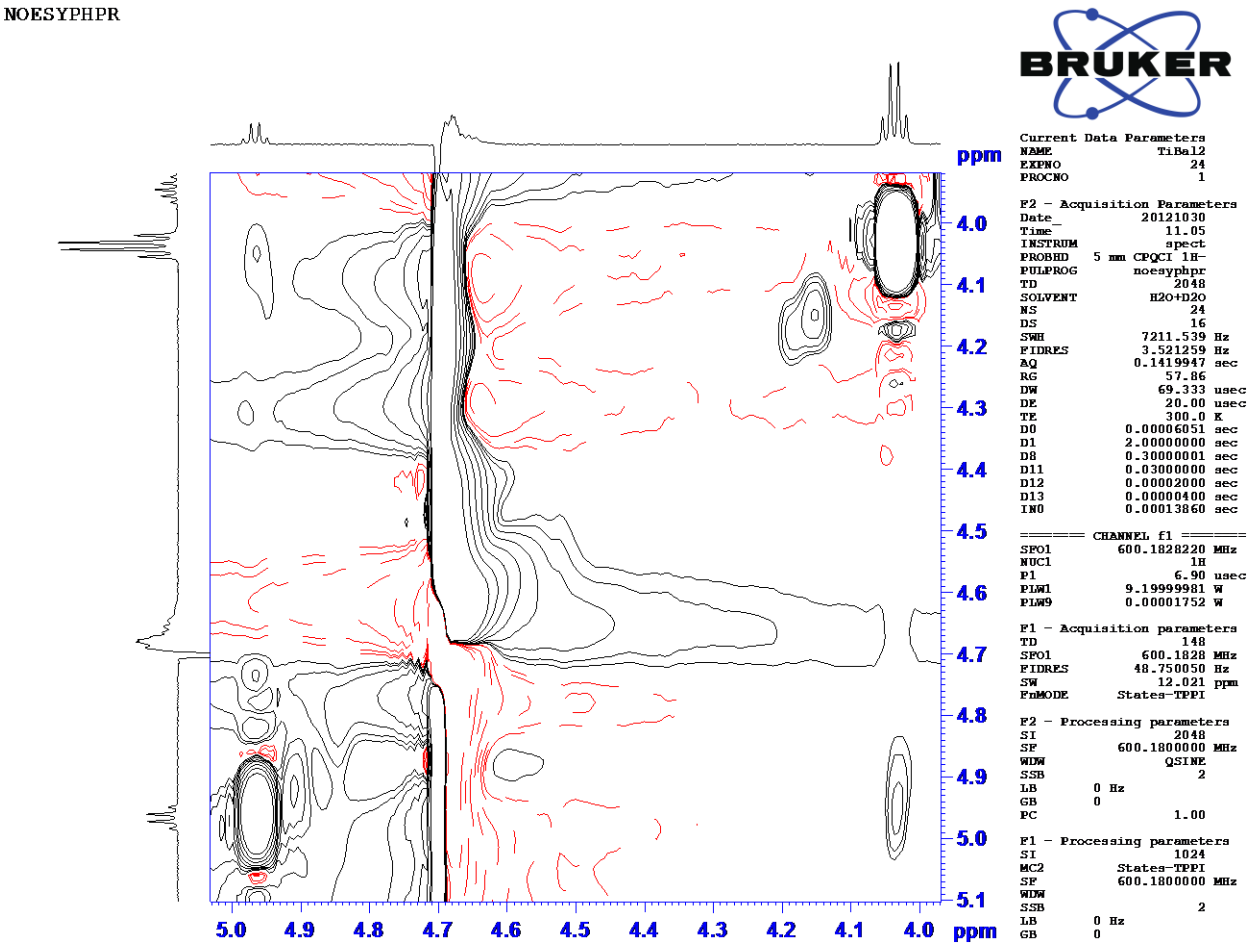


Figure FS12

NOESY spectrum of TiBALDH in the lactate CH_3-region (water signal in the text of the paper is omitted for clarity)