Supporting Information

Regioselective conversions of H_4pdta (1,2-propanediaminetetraacetic acid) and H_4eed3a to their triacetates on peroxotitanates

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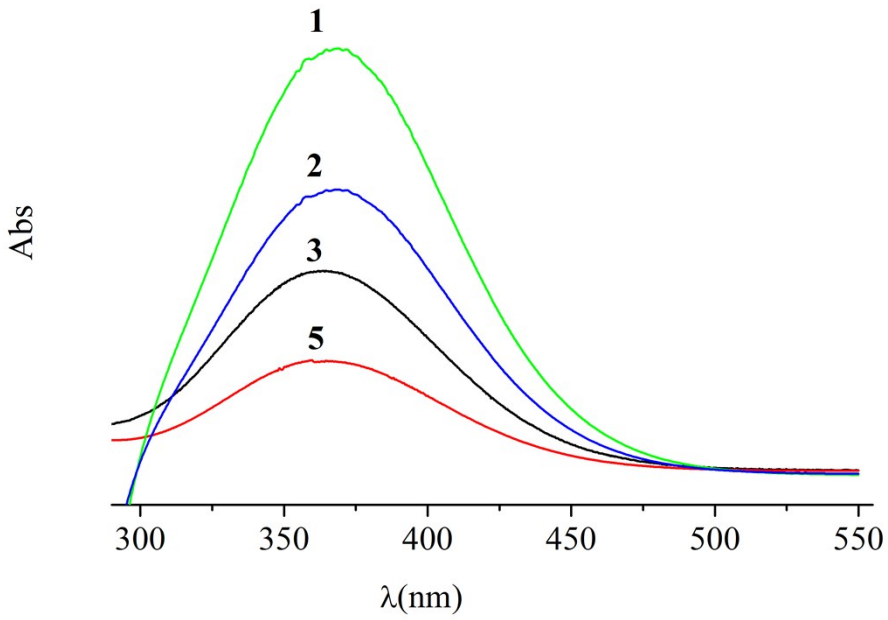
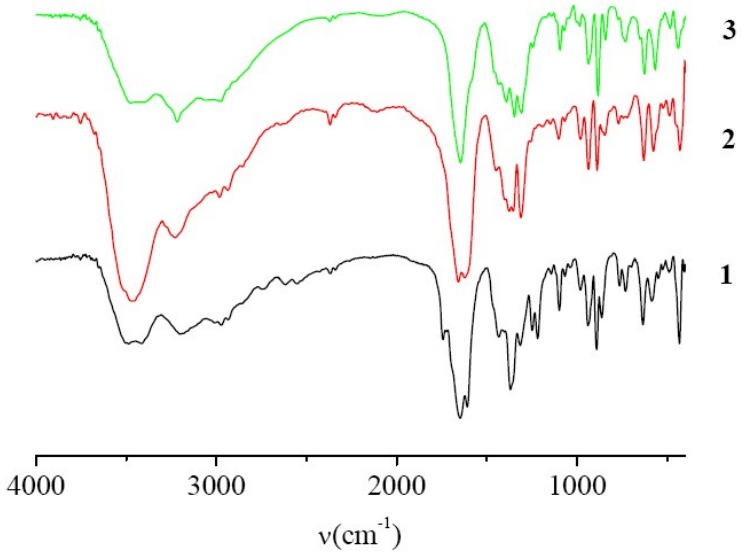
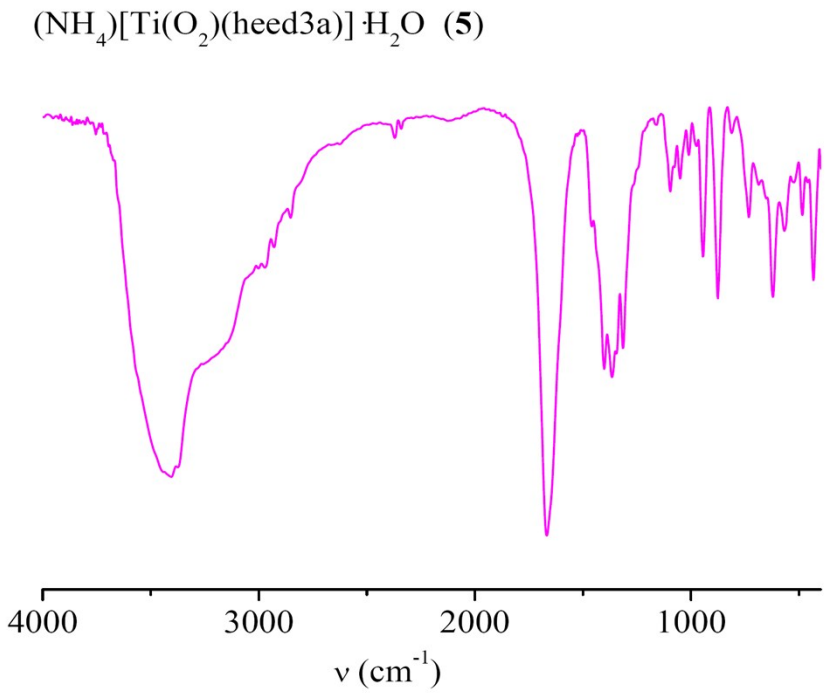
Figure S1




3
2
1
4000
3000
2000
1000
ν(cm-1)


(NH4)[Ti(O2)(heed3a)]·H2O (5)
4000
3000
2000
1000
ν (cm-1)

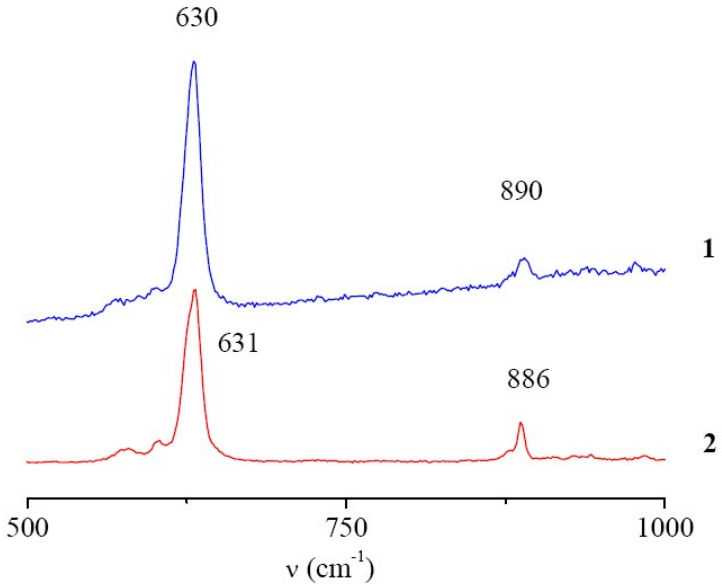

630
890
1
631
886
2
500
750
1000
ν (cm-1)

Figure S5

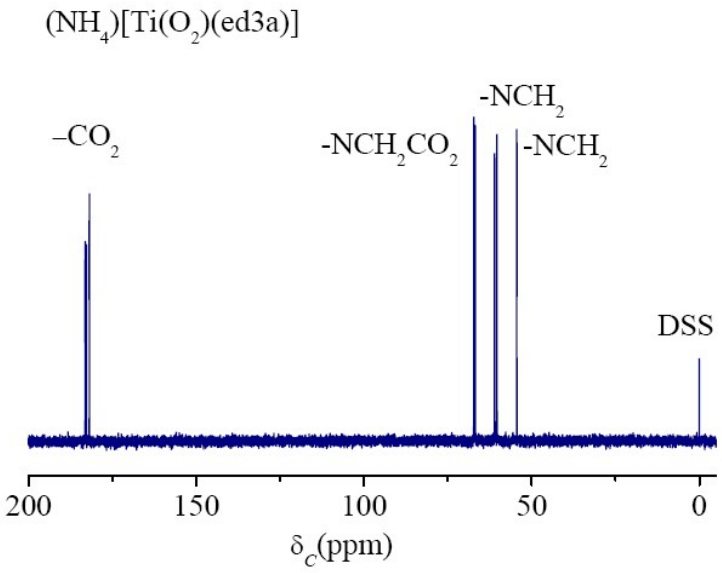


Figure S6

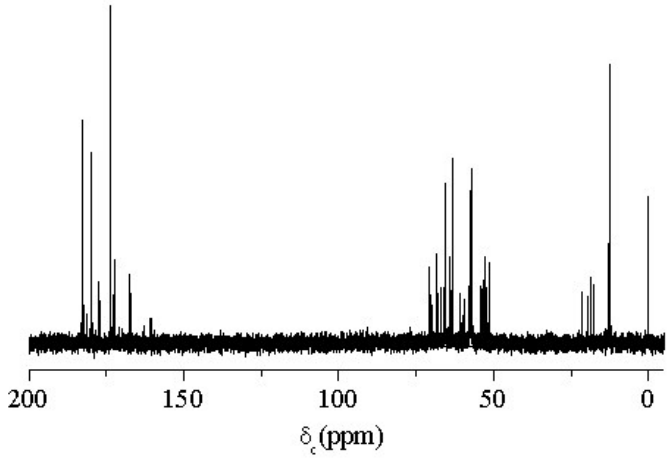
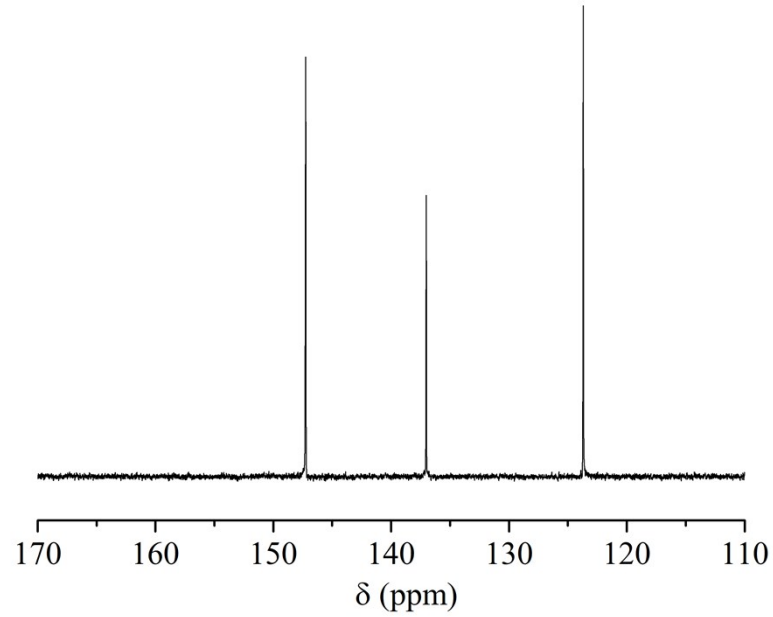


Figure S7



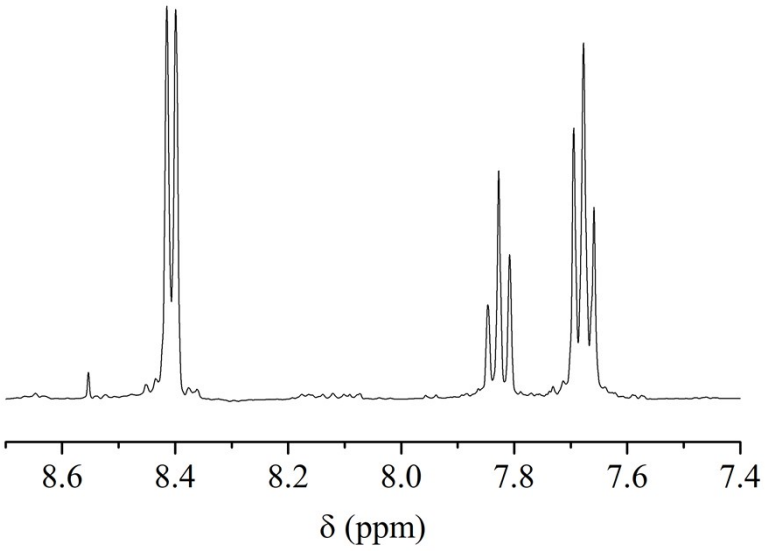
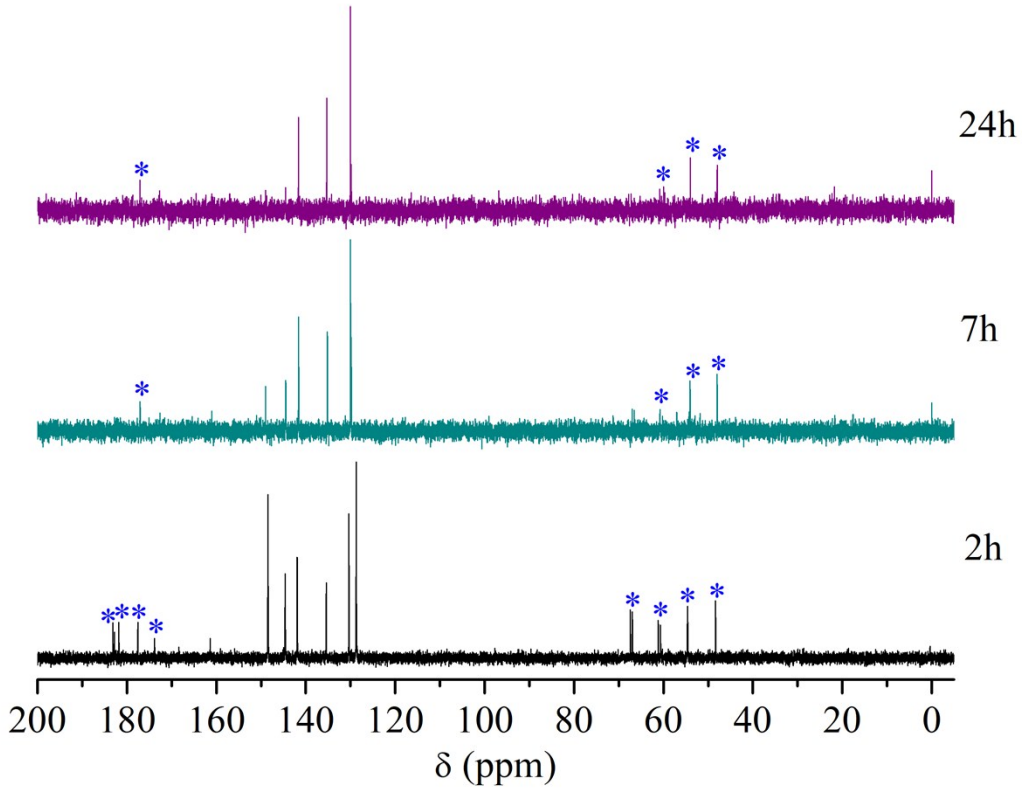


Figure S8



Scheme S1

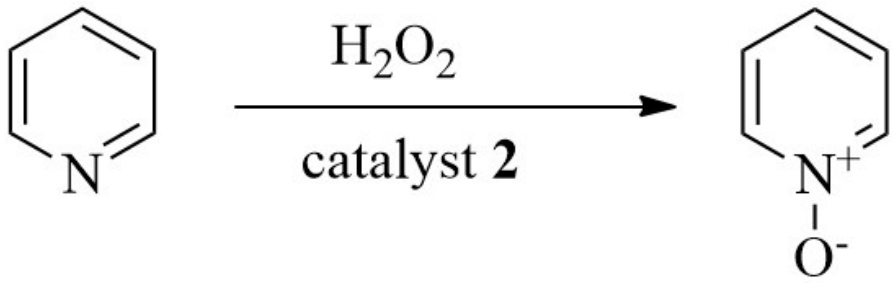


Table S1. Crystal data summaries of intensity data collections and structure refinements for $(NH_4)[Ti(O_2)(Hpdta)]\cdot H_2O$ (**1**), $(NH_4)_3[Ti(O_2)(pdta)H(pdta)(O_2)Ti]\cdot 7H_2O$ (**2**), $(NH_4)[Ti(O_2)(pd3a)]\cdot H_2O$ (**3**) and $(NH_4)[Ti(O_2)(Heed3a)]\cdot H_2O$ (**5**)

	1	**2**	**3**	**5**
Empirical formula	$C_{11}H_{21}N_3O_{11}Ti$	$C_{22}H_{55}N_7O_{27}Ti_2$	$C_9H_{19}N_3O_9Ti$	$C_{10}H_{21}N_3O_{10}Ti$
Formula weight	419.21	945.47	361.17	391.20
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
a/Å	6.6948(3)	23.00(1)	16.1839(6)	7.9665(1)
b/Å	7.5422(4)	12.077(1)	11.1970(4)	30.1390(3)
c/Å	16.7297(8)	16.442(9)	15.8291(6)	13.2150(1)
α/°	83.398(4)			
β/°	85.937(4)	124.99(4)	103.231(4)	104.765(1)
γ/°	77.802(4)			
Unit cell volume/Å^3	819.25(7)	3741(3)	2792.3(2)	3068.18(6)
Space group	$P\bar{1}$	C 2/c	C 2/c	P 2_1/a
No. of units per unit cell, Z	2	4	8	8
Temperature, K	173(2)			
Radiation type	Mo Kα			
D_{calc} (g·cm^{-3})	1.699	1.679	1.713	1.694
Absorption coefficient, μ/mm^{-1}	0.590	0.537	0.666	0.618
No. of reflections measured	10186	8458	10553	23075
No. of independent reflections	5294	4114	3195	4575
R_{int}	0.0425	0.0975	0.0443	0.0203
Final R_1 values [$I > 2\sigma(I)$]	0.0348	0.0849	0.0346	0.0129
Final $wR(F^2)$ values [$I > 2\sigma(I)$]	0.0599	0.1097	0.0720	0.0341
Final R_1 values (all data)	0.0816	0.1521	0.0565	0.0881
Final $wR(F^2)$ values (all data)	0.0651	0.1326	0.0759	0.0369
Goodness of fit on F^2	0.787	1.049	0.958	0.0896
Largest diff. peak and hole (e·Å^{-3})	0.33/-0.36	0.51/-0.59	0.76/-0.27	0.78/-0.52

Table S2. Selected bond distances (Å) and angles (º) for $(NH_4)[Ti(O_2)(Hpdta)]\cdot H_2O$ (**1**), $(NH_4)_3[Ti(O_2)(pdta)H(pdta)(O_2)Ti]\cdot 7H_2O$ (**2**), $(NH_4)[Ti(O_2)(pd3a)]\cdot H_2O$ (**3**) and $(NH_4)[Ti(O_2)(Heed3a)]\cdot H_2O$ (**5**).

Compd.	**1**	**2**	**3**	**5**
Bond lengths (Å)				
Ti (1)─O(1)	2.069(1)	1.954(4)	1.962(1)	2.048(2)
Ti (1)─O(3)	1.996(1)	2.066(3)	2.015(1)	1.979(2)
Ti (1)─O(5)	1.944(1)	1.982(4)	1.976(1)	1.962(2)
Ti (1)─O(7)			1.881(2)	
Ti (1)─O(8)			1.854(2)	1.865(2)
Ti (1)─O(9)	1.844(1)	1.835(3)		1.850(2)
Ti (1)─O(10)	1.862(1)	1.856(3)		
Ti (1)─O(1w)				
Ti (1)─N(1)	2.280(1)	2.318(4)	2.301(2)	2.286(2)
Ti (1)─N(2)	2.284(1)	2.285(4)	2.204(2)	2.272(2)
Bond angles (º)				
O(1)─Ti(1)─O(3)	92.19(4)	96.3(1)	98.62(6)	94.00(7)
O(1)─Ti(1)─O(5)	93.40(5)	157.2(1)	160.88(6)	90.90(7)
O(1)─Ti(1)─O(7)			93.49(6)	
O(1)─Ti(1)─O(8)			98.97(6)	81.03(8)
O(1)─Ti(1)─O(9)	127.00(5)	100.7(2)		127.51(8)
O(1)─Ti(1)─O(10)	80.48(5)	94.5(2)		
O(1)─Ti(1)─O(1w)				
O(1)─Ti(1)─N(1)	73.66(4)	76.2(1)	77.48(6)	73.72(7)
O(1)─Ti(1)─N(2)	151.00(5)	89.1(2)	86.89(6)	150.37(7)
O(3)─Ti(1)─O(5)	158.06(4)	86.2(1)	88.59(6)	156.95(7)
O(3)─Ti(1)─O(7)			128.79(6)	
O(3)─Ti(1)─O(8)			82.50(6)	101.20(8)
O(3)─Ti(1)─O(9)	93.84(5)	81.6(2)		94.84(8)
O(3)─Ti(1)─O(10)	99.56(5)	128.1(1)		
O(3)─Ti(1)─O(1w)				
O(3)─Ti(1)─N(1)	77.51(5)	73.4(1)	74.81(6)	77.04(8)
O(3)─Ti(1)─N(2)	87.42(4)	148.4(1)	149.09(6)	86.96(7)
O(5)─Ti(1)─O(7)			95.71(6)	
O(5)─Ti(1)─O(8)			99.52(6)	101.81(7)
O(5)─Ti(1)─O(9)	99.64(5)	102.0(2)		99.99(8)
O(5)─Ti(1)─O(10)	102.29(5)	101.7(2)		
O(5)─Ti(1)─O(1w)				
O(5)─Ti(1)─N(1)	83.72(5)	82.9(1)	87.49(6)	82.77(7)
O(5)─Ti(1)─N(2)	77.51(5)	77.6(1)	78.22(6)	77.90(7)
O(7)─Ti(1)─O(8)			46.42(6)	
O(7)─Ti(1)─O(9)				
O(7)─Ti(1)─O(10)				
O(7)─Ti(1)─O(1w)				
O(7)─Ti(1)─N(1)			156.14(6)	
O(7)─Ti(1)─N(2)			80.74(6)	
O(1w)─Ti(1)─N(1)				

O(1w)─Ti(1)─N(2)				
O(8)─Ti(1)─O(9)				46.50(8)
O(8)─Ti(1)─N(1)			156.10(6)	154.44(8)
O(8)─Ti(1)─N(2)			126.94(7)	127.87(8)
O(9)─Ti(1)─O(10)	46.59(5)	46.5(1)		
O(9)─Ti(1)─N(1)	158.38(5)	154.3(2)		158.22(8)
O(9)─Ti(1)─N(2)	81.92(5)	128.0(1)		81.77(7)
O(10)─Ti(1)─N(1)	153.79(5)	157.9(2)		
O(10)─Ti(1)─N(2)	128.18(5)	82.2(1)		
N(1)─Ti(1)─N(2)	77.96(5)	77.7(1)	76.77(6)	77.68(7)

Table S3. Geometrical parameters of hydrogen bonds (Å, degree) in $(NH_4)[Ti(O_2)(Hpdta)]\cdot H_2O$ (**1**), $(NH_4)_3[Ti(O_2)(pdta)H(pdta)(O_2)Ti]\cdot 7H_2O$ (**2**) and $(NH_4)[Ti(O_2)(Heed3a)]\cdot H_2O$ (**5**)

Compelexs.	D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	D−H···A(°)
1	O7−H···O1w	0.756(2)	1.798(2)	2.548(2)	171(3)
2	O7–H···O7a	1.225(3)	1.225(3)	2.450(6)	180(1)
5	O7−H···O16a	0.839(2)	2.004(8)	2.838(3)	172(8)
	O17−H···O6b	0.826(3)	2.032(2)	2.790(3)	152(8)

Symmetric transformation for **2**: *a*, ½ - *x*, -½ - *y*, 1 - *z*; **5**: *a*, 1 + *x, y, z* ; b, ½ + *x*, ½ - *y*, 1 + *z*

Table S4. Relevant ^{13}C NMR data, δ/ppm of H_4edta, $(NH_4)[Ti(O_2)(Hedta)]\cdot 2H_2O$, $(NH_4)_2[Ti(O_2)(edta)]\cdot 2H_2O$ and $(NH_4)[Ti(O_2)(ed3a)]$

Compounds.	$–CH_2N$	$–NCH_2CO_2$	$–COOH$ / CH_2CO_2
H_4edta	51.3	54.6	172.0
$(NH_4)[Ti(O_2)(Hedta)]\cdot 2H_2O$[11]	59.7	66.1(11.5)	179.9(7.9)
$(NH_4)_2[Ti(O_2)(edta)]\cdot 2H_2O$[11]	60.3	66.7(12.1)	180.4(8.4)
$(NH_4)[Ti(O_2)(ed3a)]$[11]	54.4, 60.3, 61.0	66.8, 67.2	181.8, 182.8, 183.1

Δδ values are given in parentheses.