

Supporting Information

Selective ligand conversion of ethylenediamine tetraacetate to its triacetate by peroxotitanate(IV)

Zhao-Hui Zhou,^{*,†} Yuan-Fu Deng,[†] Qiong-Xin Liu,[†] Hua-Lin Zhang,[†] Thomas C. W. Mak,[‡] Yuan L. Chow[†]

[†] Department of Chemistry, College of Chemistry and Chemical Engineering and State Key Laboratory for Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen, 361005, China. Fax: +86 592 2183047;

Tel: +86 592 2184531, E-mail: zhzhou@xmu.edu.cn

[‡] Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, China

Experimental Section

Physical Measurements and the Preparations of 1–3.

Infrared spectra were recorded as Nujol mulls between KBr plates with a Nicolet 360 FT-IR spectrometer. Raman spectra were carried out with a Renishaw Raman System 1000R and a laser at 514.5 nm used as the excitation source. Electronic spectra in solution were recorded on a UV 2501 spectrophotometer. Elemental analyses were performed with an EA 1110 elemental analyzer. ¹H and ¹³C NMR spectra were recorded in D₂O on a Varian UNITY 500 or a Bruker 400 NMR spectrometer using DSS (sodium 2,2-dimethyl-2-silapentane-5-sulfonate) as the internal reference.

The conditions of physical measurements are the same as those reported before.¹¹ [Ti(edta)(H₂O)] (**1**) was prepared according to the previously reported procedures.⁴ **1** (3.55 g, 10 mmol) was suspended in 10 ml of 30% hydrogen peroxide with stirring. This mixture was adjusted to pH 2.5 with dilute ammonia hydroxide and was filtered; the clear solution was evaporated at room temperature in a rotary evaporator to deposit yellow crystals of (NH₄)[Ti(O₂)(Hedta)]·2H₂O (**2**), which was filtered, washed with ethanol and dried to afford **2** (3.89 g, 92%). Elemental analysis: calcd. (%) for C₁₀H₂₁O₁₂N₃Ti: C 28.4, H 5.0, N 9.9; found C 28.1, H 5.0, N 9.9.

A solution of (**2**) (4.23 g, 10 mmol) in 5 ml of deionized water was adjusted to pH 5.5 with dilute ammonium hydroxide and filtered. The solution was evaporated at the room temperature during 8 hours. The product was filtered, washed with ethanol (95%) two times and dried in the air at room temperature to give yellow crystals of $(\text{NH}_4)_2[\text{Ti}(\text{O}_2)(\text{edta})]\cdot 2\text{H}_2\text{O}$ (**3**) (3.08g , 70%). Elemental analysis: calcd. (%) for $\text{C}_{10}\text{H}_{24}\text{O}_{12}\text{N}_4\text{Ti}$: C 27.3, H 5.5, N 12.7; found C 27.0, H 5.4, N 12.6.

*Preparations of $M[\text{Ti}(\text{O}_2)(\text{ed3a})]\cdot n\text{H}_2\text{O}$ [**4**, $M = \text{NH}_4$, $n = 0$; **5**, $M = \text{Na}$, $n = 1$].*

$[\text{Ti}(\text{edta})(\text{H}_2\text{O})]$ (**1**) (0.355 g, 1 mmol) was suspended in 1 ml of 30% hydrogen peroxide with stirring. The mixture was adjusted to pH 6.0 with dilute ammonia hydroxide, and was kept at 25 °C for two weeks to deposit yellow crystals which were filtered and washed to give $(\text{NH}_4)[\text{Ti}(\text{O}_2)(\text{ed3a})]$ (**4**) (0.201 g, 61%). Elemental analysis: calcd. (%) for $\text{C}_8\text{H}_{15}\text{O}_8\text{N}_3\text{Ti}$: C 29.2, H 4.6, N 12.8; found C 28.8, H 4.6, N 12.7. Also, $(\text{NH}_4)_2[\text{Ti}(\text{O}_2)(\text{edta})]\cdot 2\text{H}_2\text{O}$ (**3**) (0.440 g, 1 mmol) was treated under similar conditions to afford the deposit of **4** (0.263 g, 80%).

Starting from **1** (0.355 g, 1 mmol) under the same conditions but when pH was adjusted with dilute sodium hydroxide, complex $\text{Na}[\text{Ti}(\text{O}_2)(\text{ed3a})]\cdot \text{H}_2\text{O}$ (**5**) was isolated (0.183 g, 52%). Elemental analysis: calcd. (%) for $\text{C}_8\text{H}_{13}\text{O}_9\text{N}_2\text{NaTi}$: C 27.3, H 3.7, N 8.0; found C 27.0, H 3.6, N 7.6. The mother liquor remained after the isolation was evaporated at 25 °C to precipitate colorless crystals of sodium malate $\text{NaOOCCH}(\text{OH})\text{CH}_2\text{COONa}\cdot \text{H}_2\text{O}$ (**6**) (0.021 g, 21%). Elemental analysis: calcd. (%) for $\text{C}_4\text{H}_6\text{O}_6\text{Na}_2$: calcd. C 24.5, H 3.1; found C 24.3, H 3.1. The residue from the filtrate showed a clean ^{13}C NMR spectrum indicating the presence of sodium malate, glycollate, and oxalate. The physical data of **2 ~ 6** are listed as follows.

*Physical Data of **2 ~ 6***

Physical data of $(\text{NH}_4)[\text{Ti}(\text{O}_2)(\text{Hedta})]\cdot 2\text{H}_2\text{O}$ (**2**): Solution UV-Vis spectra: $\epsilon_{365} = 812$ $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$. IR (KBr): $\nu(\text{CO}_2\text{H}) = 1721$ m, $\nu_{\text{as}}(\text{CO}_2) = 1684$ vs, 1650 vs, 1594 vs, $\nu_s(\text{CO}_2) = 1385$ s, 1368 s, 1324.1 m, $\nu(\text{O}-\text{O}) = 890$ s; $\nu[\text{Ti}-(\text{O}_2)] = 629$ m cm^{-1} . Raman: $\nu(\text{O}-\text{O}) = 890$ m, $\nu[\text{Ti}-(\text{O}_2)] = 628$ vs cm^{-1} . ^1H NMR (500 MHz): $\delta = 4.112$ (b, 8H, CH_2CO_2^-), 3.344 (b, 4H, $\text{N}-\text{CH}_2$) ppm. ^{13}C NMR (125 MHz) $\delta = 179.9$ (CO_2), 66.1 ($-\text{CH}_2\text{CO}_2$), 59.7 ($\text{N}-\text{CH}_2$) ppm.

Physical data of $(\text{NH}_4)_2[\text{Ti}(\text{O}_2)(\text{edta})]\cdot 2\text{H}_2\text{O}$ (**3**): Solution UV-Vis spectra: $\epsilon_{365} = 899$ $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$. IR (KBr): $\nu_{\text{as}}(\text{CO}_2) = 1655$ vs, 1604 m; $\nu_s(\text{CO}_2) = 1399$ s, 1347 m; $\nu(\text{O}-\text{O}) =$

888 m; $\nu[\text{Ti}-(\text{O}_2)] = 627 \text{ m cm}^{-1}$. Raman: $\nu(\text{O}-\text{O}) = 887 \text{ m}, \nu[\text{Ti}-(\text{O}_2)] = 626 \text{ vs cm}^{-1}$. ^1H NMR (500 MHz): $\delta = 4.101$ (d, $J 17.0 \text{ Hz}$, 4H, CH_2), 4.023 (d, $J 16.0 \text{ Hz}$, 4H, CH_2), 3.333 (b, 4H, $\text{N}-\text{CH}_2$) ppm. ^{13}C NMR (125 MHz) $\delta = 180.4$ (CO_2) 66.7 ($-\text{CH}_2\text{CO}_2$), 60.3 ($\text{N}-\text{CH}_2$) ppm.

Physical data of $(\text{NH}_4)[\text{Ti}(\text{O}_2)(\text{ed}3\text{a})]$ (**4**): Solution UV-Vis Spectra: $\varepsilon_{363} = 1383 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$. IR (KBr): $\nu_{\text{as}}(\text{CO}_2) = 1640 \text{ vs}, 1613 \text{ vs}, \nu_{\text{s}}(\text{CO}_2) = 1432 \text{ m}, 1395 \text{ m}, 1319 \text{ s}, \nu(\text{O}-\text{O}) = 884 \text{ s}, 867 \text{ s}, \nu[\text{Ti}-(\text{O}_2)] = 629 \text{ m cm}^{-1}$. Raman: $\nu(\text{O}-\text{O}) = 885 \text{ m}, \nu[\text{Ti}-(\text{O}_2)] = 627 \text{ vs cm}^{-1}$. ^1H NMR (500 MHz): $\delta = 4.604$ (d, $J 18.0 \text{ Hz}$, 1H, CH_2), 4.023 (d, $J 18.5 \text{ Hz}$, 1H, CH_2); 3.849 (d, $J 7.5 \text{ Hz}$, 1H, CH_2), 3.814 (d, $J 7.5 \text{ Hz}$, 1H, CH_2); 3.679 (d, $J 17.0 \text{ Hz}$, 1H, CH_2), 3.632 (d, $J 18.0 \text{ Hz}$, 1H, CH_2), 3.111–3.357 (m, 4H, $\text{N}-\text{CH}_2$) ppm. ^{13}C NMR (125 MHz) $\delta = 183.1, 182.8 (= \text{NCH}_2\text{CO}_2), 181.8 [-\text{HNCH}_2(\text{CO}_2)], 67.2, 66.8 (-\text{CH}_2\text{CO}_2), 61.0, 60.3 (= \text{NCH}_2), 54.4 (-\text{HNCH}_2)$ ppm.

Physical data of $\text{Na}[\text{Ti}(\text{O}_2)(\text{ed}3\text{a})]\cdot\text{H}_2\text{O}$ (**5**): Solution UV-Vis Spectra: $\varepsilon_{364} = 1420 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$. IR (KBr): $\nu_{\text{as}}(\text{CO}_2) = 1678 \text{ vs}, 1639 \text{ vs}, \nu_{\text{s}}(\text{CO}_2) = 1363 \text{ s}, 1306 \text{ s}, \nu(\text{O}-\text{O}) = 884 \text{ s}, 868 \text{ s}, \nu[\text{Ti}-(\text{O}_2)] = 633 \text{ m cm}^{-1}$. Raman: $\nu(\text{O}-\text{O}) = 885 \text{ m}, \nu[\text{Ti}-(\text{O}_2)] = 626 \text{ vs cm}^{-1}$. ^1H NMR (400 MHz): $\delta = 4.639$ (d, $J 18.0 \text{ Hz}$, 1H, CH_2), 4.055 (d, $J 18.4 \text{ Hz}$, 1H, CH_2); 3.891 (d, $J 3.6 \text{ Hz}$, 1H, CH_2), 3.847 (d, $J 6.0 \text{ Hz}$, 1H, CH_2); 3.711 (d, $J 16.0 \text{ Hz}$, 1H, CH_2), 3.689 (d, $J 18.0 \text{ Hz}$, 1H, CH_2), 3.148–3.413 (m, 4H, $\text{N}-\text{CH}_2$) ppm. ^{13}C NMR (100 MHz) $\delta = 183.1, 182.7 (= \text{NCH}_2\text{CO}_2), 181.7 [-\text{HNCH}_2\text{CO}_2], 67.2, 66.8 (-\text{CH}_2\text{CO}_2), 60.9, 60.3 (= \text{NCH}_2), 54.4 (-\text{HNCH}_2)$ ppm.

Physical data of sodium malate $\text{NaOOCC}(\text{OH})\text{CH}_2\text{COONa}\cdot\text{H}_2\text{O}$ (**6**): IR (KBr): $\nu_{\text{as}}(\text{CO}_2) = 1608 \text{ vs}, 1587 \text{ vs}, \nu_{\text{s}}(\text{CO}_2) = 1408 \text{ s}, 1378 \text{ s}, \text{cm}^{-1}$. ^1H NMR (400 MHz): $\delta = 4.304$ (d, $J 9.6, 3.2 \text{ Hz}$, 1H, CH), 2.678 (d, $J 15.6, 3.2 \text{ Hz}$, 1H, CH_2); 2.409 (d, $J 15.6, 9.6 \text{ Hz}$, 1H, CH_2) ppm. ^{13}C NMR (100 MHz) $\delta = 183.9 (\alpha\text{-CO}_2), 182.7 (\beta\text{-CO}_2), 73.0 (= \text{CHCO}_2), 45.3 (= \text{CH}_2)$ ppm.

Figure Options

- Figure S1. Solution UV-Vis spectra of peroxotitanium(IV) complexes: $(\text{NH}_4)[\text{Ti}(\text{O}_2)(\text{Hedta})]\cdot 2\text{H}_2\text{O}$ (**2**), $(\text{NH}_4)_2[\text{Ti}(\text{O}_2)(\text{edta})]\cdot 2\text{H}_2\text{O}$ (**3**) and $(\text{NH}_4)[\text{Ti}(\text{O}_2)(\text{ed3a})]$ (**4**).
- Figure S2. IR spectra of peroxotitanium(IV) complexes: $[\text{Ti}(\text{edta})(\text{H}_2\text{O})]$ (**1**), $(\text{NH}_4)[\text{Ti}(\text{O}_2)(\text{Hedta})]\cdot 2\text{H}_2\text{O}$ (**2**), $(\text{NH}_4)_2[\text{Ti}(\text{O}_2)(\text{edta})]\cdot 2\text{H}_2\text{O}$ (**3**) and $(\text{NH}_4)[\text{Ti}(\text{O}_2)(\text{ed3a})]$ (**4**).
- Figure S3. Raman spectra of peroxotitanium(IV) complexes: $(\text{NH}_4)[\text{Ti}(\text{O}_2)(\text{Hedta})]\cdot 2\text{H}_2\text{O}$ (**2**), $(\text{NH}_4)_2[\text{Ti}(\text{O}_2)(\text{edta})]\cdot 2\text{H}_2\text{O}$ (**3**) and $(\text{NH}_4)[\text{Ti}(\text{O}_2)(\text{ed3a})]$ (**4**).
- Figure S4. Ortep plot of the anion structure of complex $(\text{NH}_4)[\text{Ti}(\text{O}_2)(\text{Hedta})]\cdot 2\text{H}_2\text{O}$ (**2**). Selected bond lengths (Å): Ti1–O1 1.847(1), Ti1–O2 1.848(1), Ti1–O3 2.086(1), Ti1–O5 1.986(1), Ti1–O7 1.948(1), Ti1–N1 2.294(1), Ti1–N2 2.300(1), O1–O2 1.467(2).
- Figure S5. Ortep plot of the anion structure of complex $\text{Na}[\text{Ti}(\text{O}_2)(\text{ed3a})]\cdot \text{H}_2\text{O}$ (**5**). Selected bond lengths (Å): Ti1–O1 1.855(1), Ti1–O2 1.865(1), Ti1–O3 2.032(1), Ti1–O5 1.978(1), Ti1–O7 1.989(1), Ti1–N1 2.284(2), Ti1–N2 2.219(1), O1–O2 1.466(2).
- Figure S6. Ortep plots of sodium malate $\text{NaOOCH}(\text{OH})\text{CH}_2\text{COONa}\cdot \text{H}_2\text{O}$ (**6**). Selected bond lengths (Å): C1–O1 1.420(2), C1–C2 1.524(2), C1–C3 1.516(2), C2–O2 1.256(2), C2–O3 1.245(2), C3–C4 1.517(2), C4–O4 1.259(2), C4–O5 1.249(2), Na1–O1 2.405(1), Na1–O2 2.562(2), Na2–O1 2.381(1), Na2–O5 2.394(1).
- Figure S7. ^{13}C NMR spectra of peroxotitanium(IV) complex $(\text{NH}_4)[\text{Ti}(\text{O}_2)(\text{Hedta})]\cdot 2\text{H}_2\text{O}$ (**2**).
- Figure S8. ^{13}C NMR spectra of peroxotitanium(IV) complex $(\text{NH}_4)_2[\text{Ti}(\text{O}_2)(\text{edta})]\cdot 2\text{H}_2\text{O}$ (**3**).
- Figure S9. ^{13}C NMR spectra of peroxotitanium(IV) complex **4**.
- Figure S10. Solution UV-Vis spectra of sodium peroxotitanium(IV) complex $\text{Na}[\text{Ti}(\text{O}_2)(\text{ed3a})]\cdot \text{H}_2\text{O}$ (**5**).
- Figure S11. IR spectrum of sodium peroxotitanium(IV) complex $\text{Na}[\text{Ti}(\text{O}_2)(\text{ed3a})]\cdot \text{H}_2\text{O}$ (**5**).
- Figure S12. IR spectrum of sodium malate $\text{NaOOCH}(\text{OH})\text{CH}_2\text{COONa}\cdot \text{H}_2\text{O}$ (**6**).
- Figure S13. ^{13}C NMR spectrum of sodium peroxotitanium(IV) complex $\text{Na}[\text{Ti}(\text{O}_2)(\text{ed3a})]\cdot \text{H}_2\text{O}$ (**5**).
- Figure S14. ^{13}C NMR spectrum of sodium malate $\text{NaOOCH}(\text{OH})\text{CH}_2\text{COONa}\cdot \text{H}_2\text{O}$ (**6**).
- Figure S15. ^{13}C NMR spectrum of mother liquor remained after the isolations **5** and **6**.

Figure S1

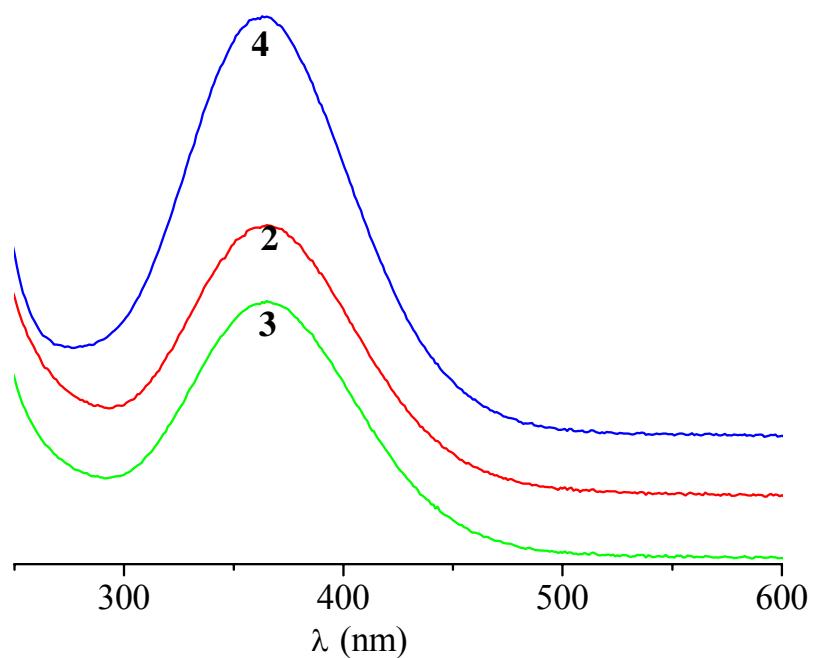
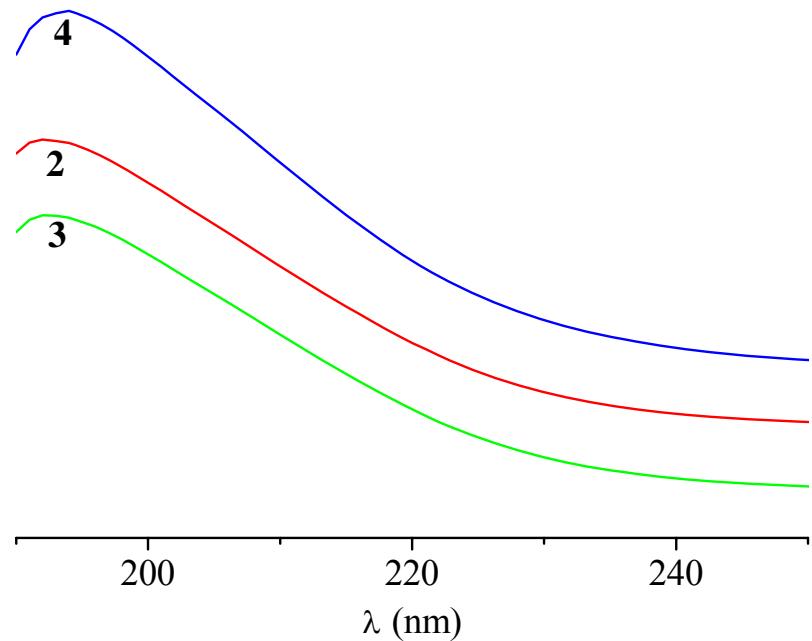


Figure S2

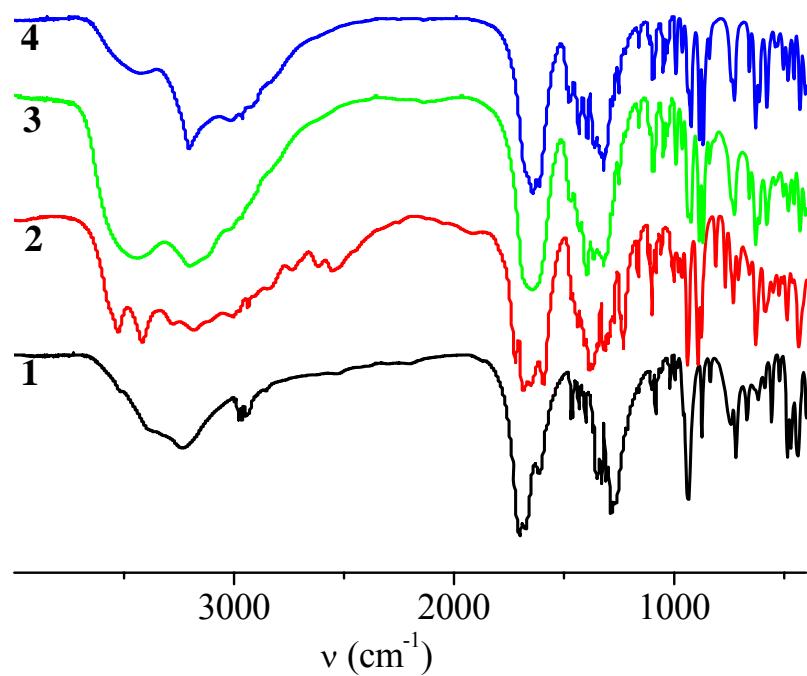


Figure S3

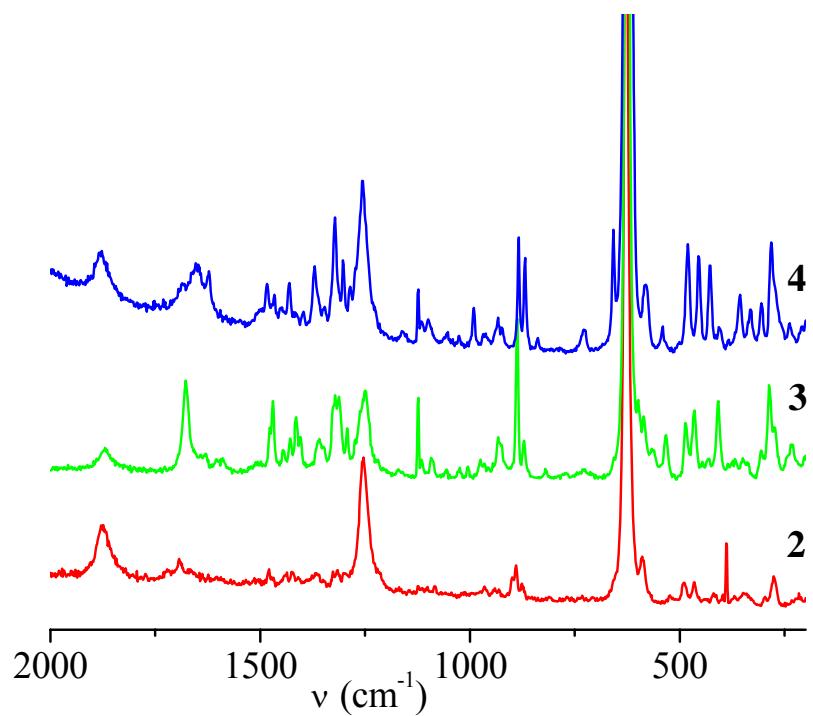


Figure S4

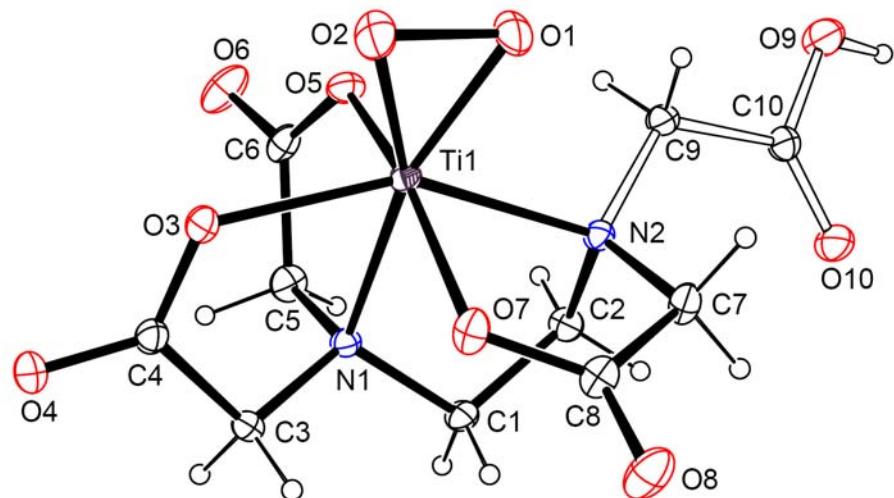


Figure S5

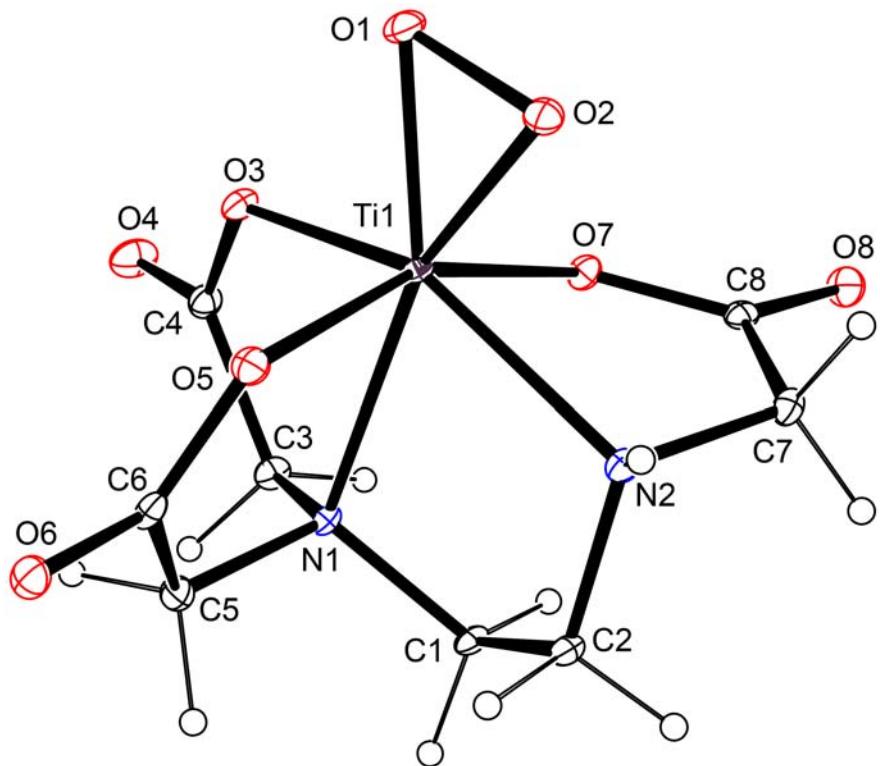


Figure S6

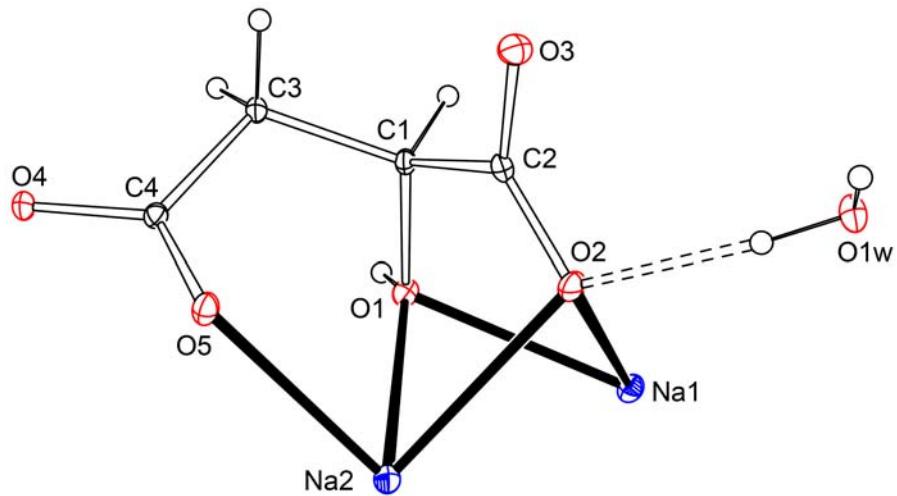


Figure S7

$(\text{NH}_4)[\text{Ti}(\text{O}_2)(\text{Hedta})] \cdot 2\text{H}_2\text{O}$ **2**

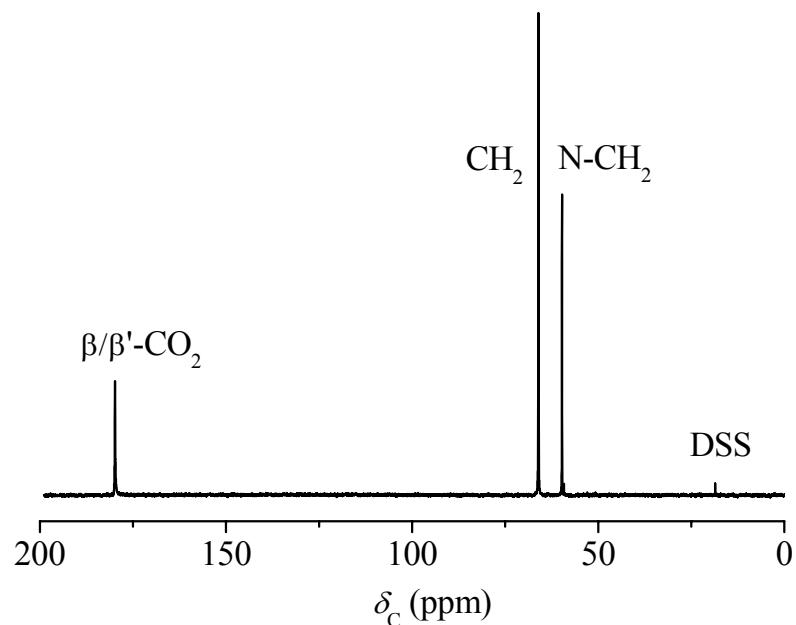


Figure S8

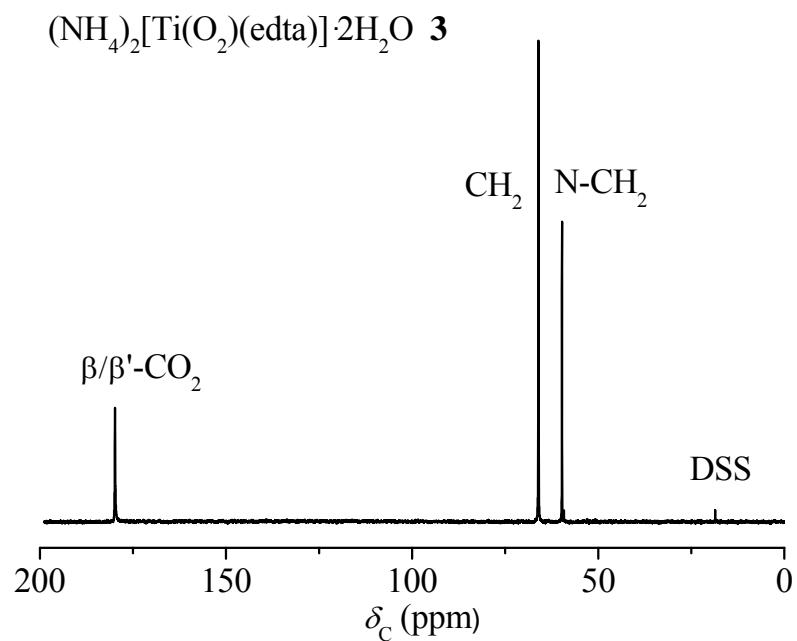


Figure S9

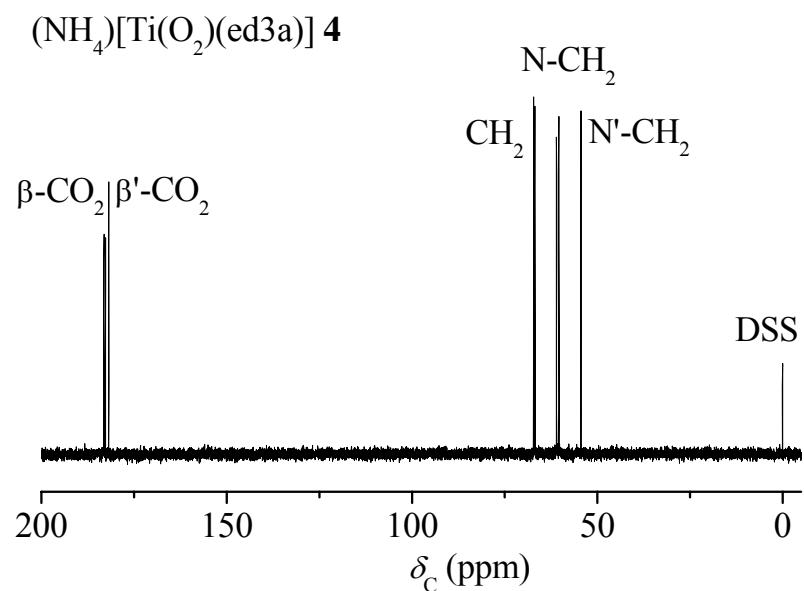


Figure S10

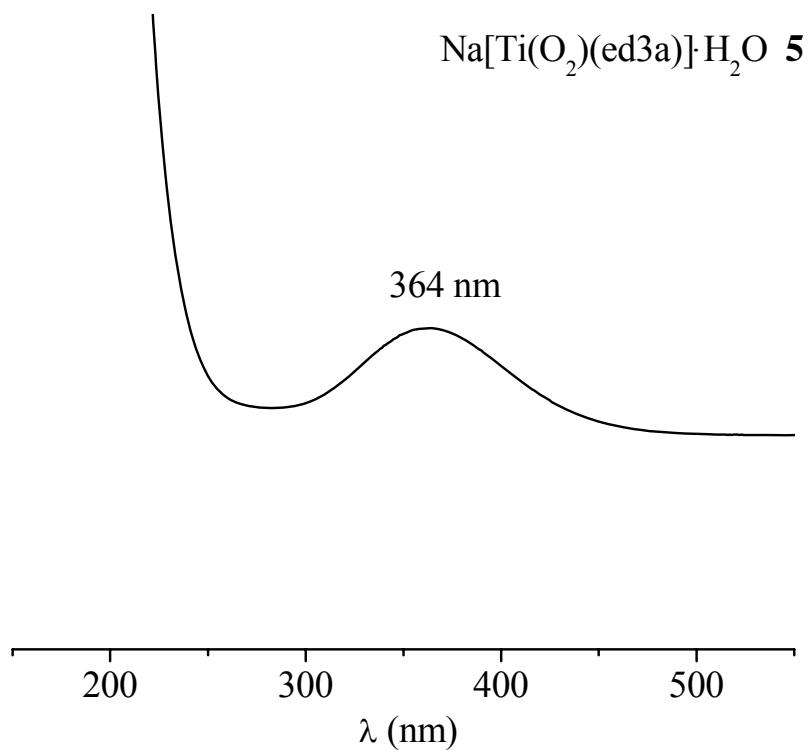


Figure S11

$\text{Na}[\text{Ti}(\text{O}_2)(\text{ed}3\text{a})]\cdot\text{H}_2\text{O}$ **5**

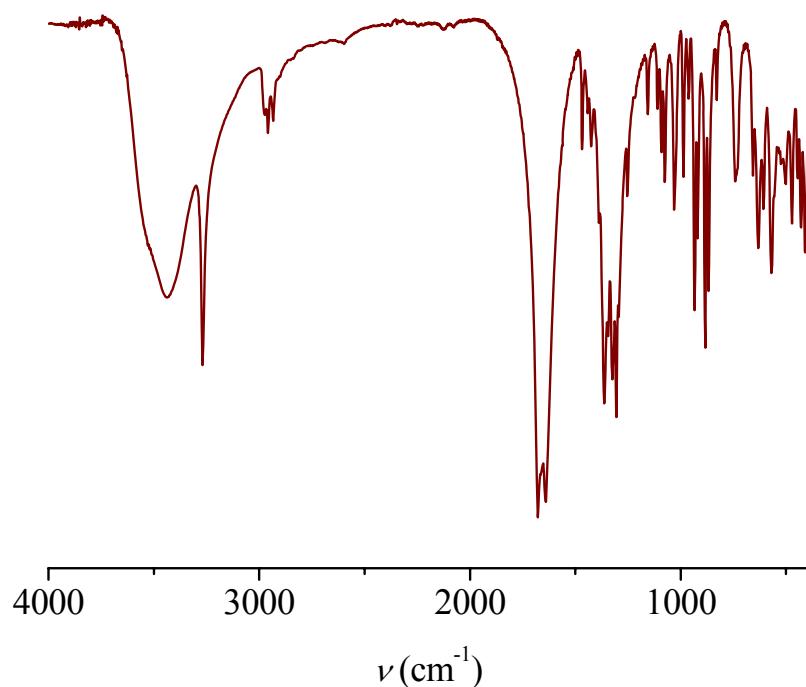


Figure S12

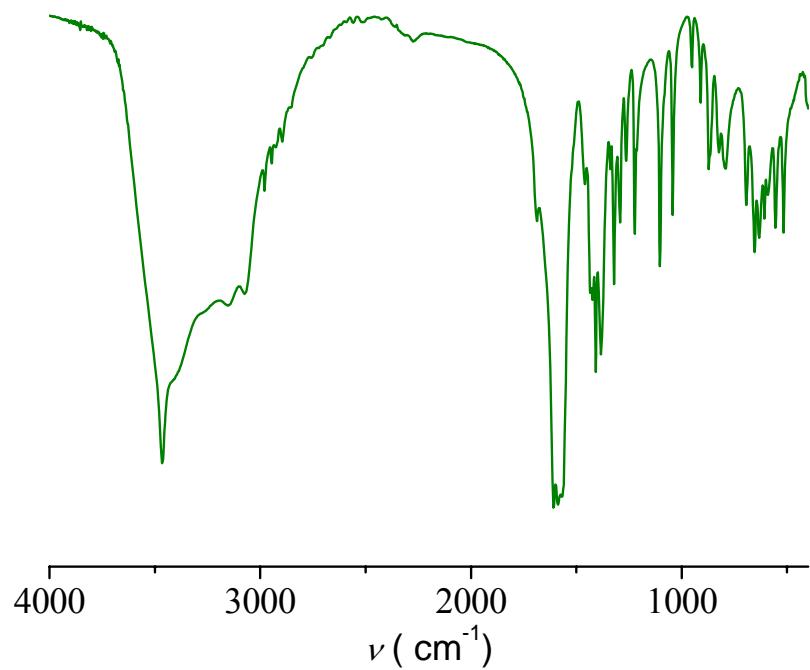


Figure S13

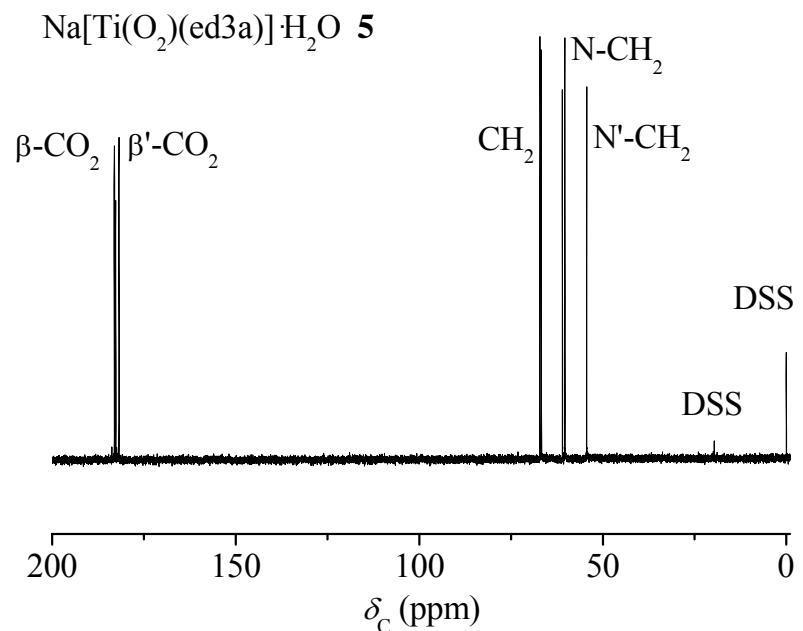


Figure S14

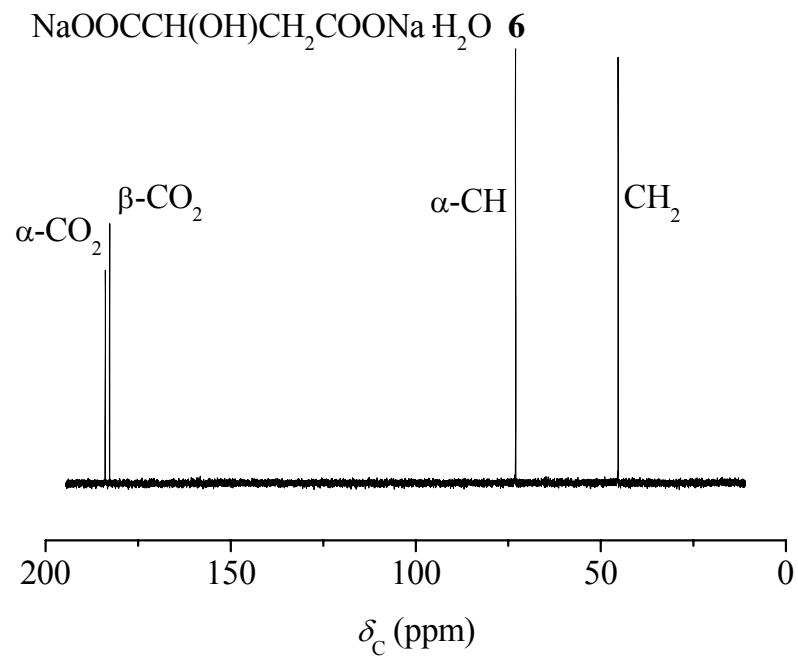


Figure S15

