Supporting information

Instrumentation information

1. Single-crystal X-ray diffractometer:
   Single-crystal X-ray diffraction intensity data were collected on a Bruker APEX DUO diffractometer equipped with a CCD area detector and Mo and Cu Kα radiation ($\lambda = 0.71073$ Å and 1.54178 Å, respectively); all data calculations were performed by using the PC version of the SHELXTL programme package.

2. Powder X-ray diffractometer:
   Room-temperature powder diffraction patterns were measured on a Bruker D2 PHASER desktop diffractometer at 300 W (30 kV, 10 mA) of power.

3. Superconducting quantum interference device (SQUID) magnetometer:
   Magnetic data were collected using a Quantum Design MPMS 5 SQUID magnetometer.

4. Electron paramagnetic resonance (EPR) spectrometer:
   X-band EPR spectra of powdered samples were recorded with a Bruker Elexsys E-580 spectrometer.

5. UV-Vis absorption spectrometer:
   UV-Vis absorption spectra of powdered samples were recorded with a Hitachi U-3010 spectrophotometer.

6. Gas chromatography (GC)
   Data were collected using a C-9800 Gas Chromatography Tester (GBPI Packaging Instrument Co., Ltd) with a high sensitivity thermal conductivity detector (TCD).

7. Nuclear magnetic resonance (NMR) spectrometer
   The solution ^{13}C NMR spectra were recorded with a Bruker Vertex 80v spectrometer.

Experimental section

1. H_2 production

Powdered samples of β-III (6.48 g, 28.56 mmol) were placed in 250 mL serum bottles capped with transfer valves, with an inlet tube for purging gas and a tube connected to a TCD for gas analysis. Each serum bottle was placed in an oil bath on a hot plate and purged with N_2 for 60 minutes before starting GC measurement. The hot plate was then set at 150°C for the thermal treatment of β-III. TCD response curves of the produced and carrier gases were recorded over the course of two hours. The amount of H_2 was about 5 μmol based on the area of GC-TCD curves, yielding the conversion degree of β-III to β-IV to be 0.03%. It is extremely a low value as the oxidation was running very slowly under the measuring condition, the sample nearly unchanged maintaining its original color after two hours, as shown in the following photo.

2. Photochemical reduction

Photochemical reduction was performed using an L-X1000 Xenon light source (Hong Ming Technology Co., Ltd., Taiwan). In a typical experiment, a powder sample of α-III or β-III (1 mmol) was dispersed in ethylene glycol in a 20-mL vial containing a stir bar, then irradiated while stirring for three days at a distance of approximately 28 cm from the lamp aperture. Afterwards, powdered samples were separated by centrifugation and characterised by PXRD. The filtrate was collected for ^{13}C solution NMR measurement.

Table S1. Crystal data and refinement results for α-III and α-IV

Compound name	α-III	α-IV
Chemical formula	$TiP_2O_7H_5$	$TiP_2O_7H_4$
Formula weight	226.88	225.87
Temperature (K)	296(2)	
Wavelength (Å)	0.71073	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 5.0662(2) Å	a = 5.0907(3) Å
	b = 12.5792(8) Å	b = 12.1407(7) Å
	c = 10.2257(6) Å	c = 10.2327(6) Å
	β = 100.078(3)°	β = 102.663(3)°
Volume (Å^3)	641.62(6)	617.05(6)
Z	4	
Density (calculated) (Mg/m^3)	2.349	2.431
Absorption coefficient (mm^{-1})	1.815	1.886
F(000)	452	448
Crystal size (mm^3)	0.05 × 0.06 × 0.16	0.06 × 0.06 × 0.23
Theta range of data collection	2.591 to 28.404°	2.641 to 28.296°
Index ranges	$-6 \le h \le 6$, $-15 \le k \le 16$, $-12 \le l \le 13$	$-4 \le h \le 6$, $-15 \le k \le 16$, $-13 \le l \le 13$
Reflections collected	6002	8309
Independent reflections	1600 [R(int) = 0.0326]	1533 [R(int) = 0.0395]
Completeness (%)	100.0	100.0
Max. and min. transmission	0.9485 and 0.8331	0.9485 and 0.8741
Data / restraints / parameters	1600 / 114 / 128	1533 / 216 / 134
Goodness-of-fit on F^2	1.118	1.128
Final R indices [I>2sigma(I)]	$R1$ = 0.0258, $wR2$ = 0.0682	$R1$ = 0.0399, $wR2$ = 0.0957
Largest diff. peak and hole (e·Å^{-3})	0.414 and -0.401	0.573 and -0.640

Table S2. Crystal data and refinement results for β-III and β-IV

Compound name	β-III	β-IV
Chemical formula	$TiP_2O_7H_5$	$TiP_2O_7H_4$
Formula weight	226.88	225.87
Temperature (K)	296(2)	
Wavelength (Å)	0.71073	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 7.4859(6) Å	a = 7.067(1) Å
	b = 7.5154(6) Å	b = 7.383(1) Å
	c = 12.1997(10) Å	c = 12.099(2) Å
	β = 102.801(2)°	β = 102.341(4)°
Volume (Å^3)	669.3(1)	616.7(2)
Z	4	
Density (calculated) (Mg/m^3)	2.252	2.433
Absorption coefficient (mm^{-1})	1.740	1.887
F(000)	452	448
Crystal size (mm^3)	0.05 × 0.05 × 0.19	0.10 × 0.10 × 0.18
Theta range of data collection	2.933 to 28.305°	3.083 to 28.328°
Index ranges	$-9 \leq h \leq 9$, $-8 \leq k \leq 10$, $-16 \leq l \leq 16$	$-9 \leq h \leq 9$, $-9 \leq k \leq 9$, $-16 \leq l \leq 16$
Reflections collected	5715	5412
Independent reflections	1645 [R(int) = 0.0234]	1518 [R(int) = 0.0243]
Completeness (%)	99.8	99.4
Max. and min. transmission	0.9485 and 0.8937	0.7457 and 0.6813
Data / restraints / parameters	1645 / 114 / 128	1518 / 0 / 91
Goodness-of-fit on F^2	1.094	1.154
Final R indices [I>2sigma(I)]	$R1$ = 0.0395, $wR2$ = 0.0840	$R1$ = 0.0362, $wR2$ = 0.0965
Largest diff. peak and hole (e·Å^{-3})	1.331 and -0.867	1.112 and -0.484

Table S3. Selected bond lengths, bond valence sums (ΣS^{*}) of Ti ions and distortions (Δ^{**}) of Ti-O octahedra for α-III and α-IV

α-III			α-IV		
Ti1	Bond length (Å)	Bond valence, S	Ti1	Bond length (Å)	Bond valence, S
O1	1.973(2)	0.61	O1	1.934(3)	0.72
O2	2.062(1)	0.48	O2	1.950(3)	0.69
O3	2.029(2)	0.52	O3	1.978(3)	0.64
O4	1.997(6)	0.57	O4	1.926(13)	0.74
O5	2.037(6)	0.51	O5	1.970(16)	0.66
O7	2.086(1)	0.45	O7	1.953(3)	0.69
ΣS(Ti-O) = 3.14, $\Delta = 3.4 \times 10^{-4}$			ΣS(Ti-O) = 4.14, $\Delta = 0.9 \times 10^{-4}$		
P1			P1		
O1	1.517(2)		O1	1.519(3)	
O2	1.524(2)		O2	1.525(3)	
O3	1.530(2)		O3	1.529(3)	
P2			P2		
O4	1.506(6)		O4	1.541(9)	
O5	1.499(6)		O5	1.510(10)	
O6	1.534(6)		O6	1.483(8)	

[*] Bond valence sums (ΣS) = $\Sigma \exp[(r_0 - r_i)/B]$, where $r_0 = 1.791$ for Ti^{3+} and 1.815 for Ti^{4+}, B = 0.37

[**] Distortion of Ti-O octahedra $\Delta = (\Sigma\, [(r_i - r_m)/r_m]^2)/6$, where r_m = mean octahedral Ti-O distance

Table S4. Selected bond lengths, bond valence sums of Ti ions and distortions of Ti-O octahedra for β-III and β-IV

β-III			β-IV		
Ti1	Bond length (Å)	Bond valence, S	Ti1	Bond length (Å)	Bond valence, S
O1	1.976(2)	0.61	O1	1.916(2)	0.76
O2	1.973(3)	0.61	O2	1.912(2)	0.77
O3	2.031(3)	0.52	O3	1.984(2)	0.63
O4	2.026(9)	0.53	O4	1.879(2)	0.84
O5	2.046(15)	0.50	O5	1.872(2)	0.86
O7	2.110(2)	0.42	O7	2.042(2)	0.54
ΣS(Ti-O) = 3.19 $\Delta = 5.2 \times 10^{-4}$			ΣS(Ti-O) = 4.40 $\Delta = 9.7 \times 10^{-4}$		
P1			P1		
O1	1.502(3)		O1	1.516(2)	
O2	1.495(3)		O2	1.516(2)	
O3	1.518(3)		O3	1.521(2)	
P2			P2		
O4	1.493(8)		O4	1.535(2)	
O5	1.494(8)		O5	1.547(2)	
O6	1.540(7)		O6	1.474(3)	

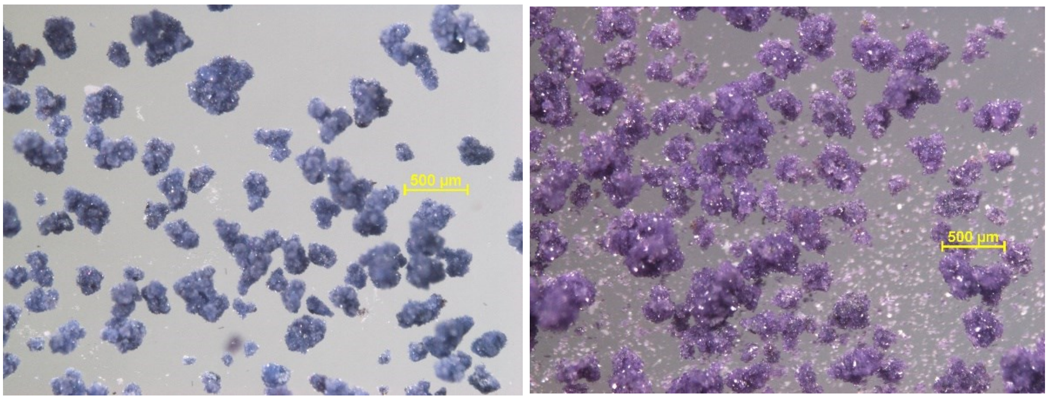

Figure S1. Photos of single-phased products for α-III (left) and β-III (right).

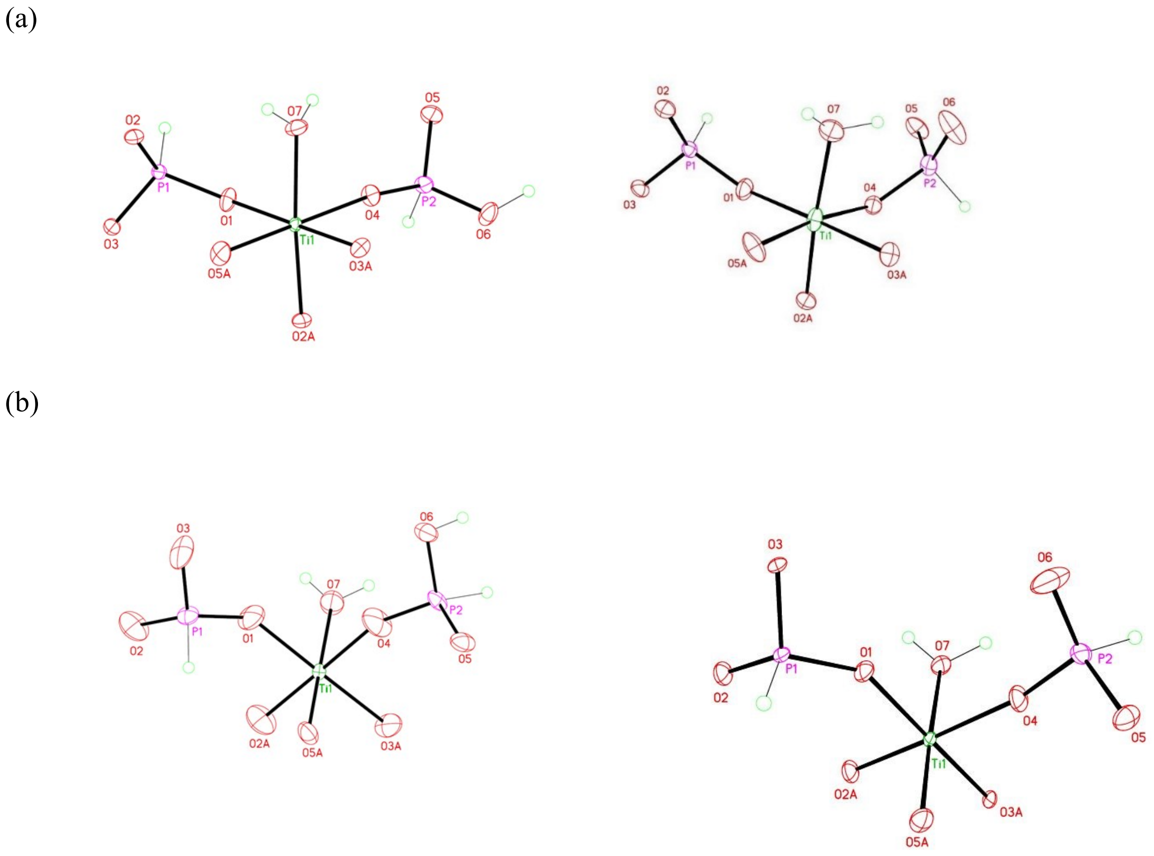

Figure S2. ORTEP for two polymorphs of Ti(H_2O)(HPO_3)(H_2PO_3): (a) α-III (left) and α-IV (right); (b) β-III (left) and β-IV (right). The thermal ellipsoids are drawn at 50% probability.

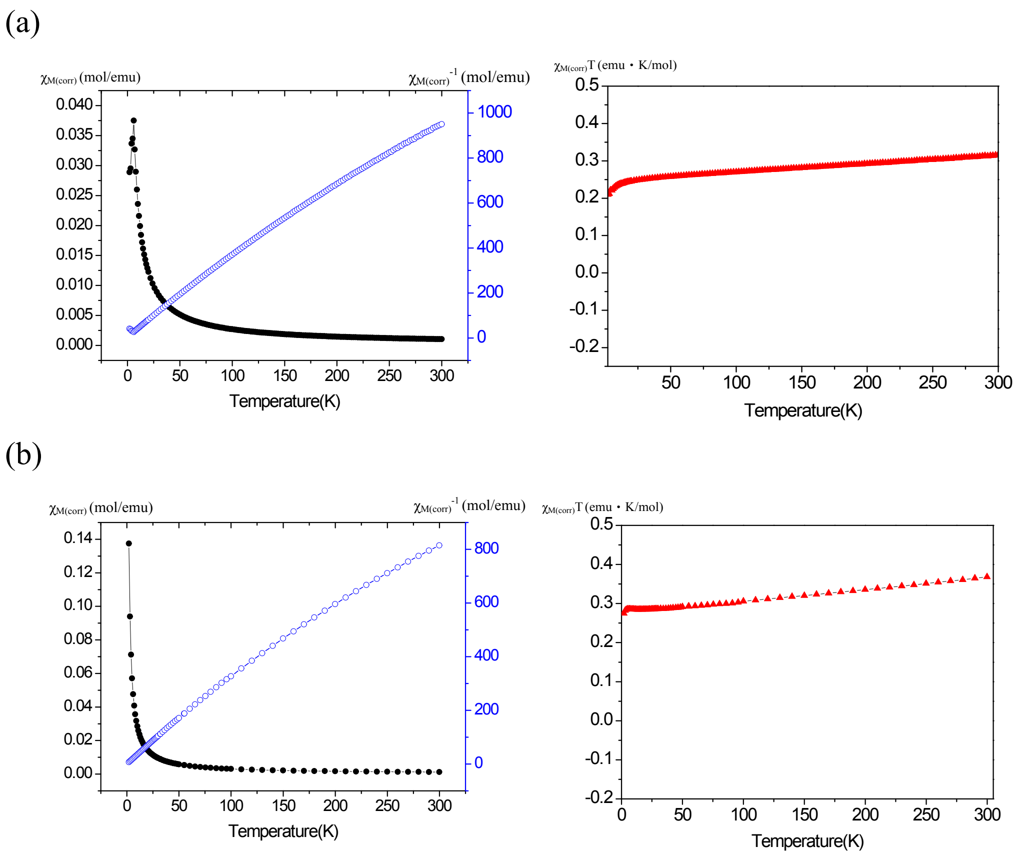

Figure S3. Temperature-dependent magnetic susceptibility data: (a) χ_M vs. T, χ_M^{-1} vs. T (left) and χ_MT vs. T (right) for α-III; (b) χ_M vs. T, χ_M^{-1} vs T (left) and χ_MT vs. T (right) for β-III. The magnetic data were analysed and fitted based on Curie-Weiss behaviour: $\chi_M = C/(T-\theta)$. The Curie constants (C in cm^{3}K/mol) and Weiss temperatures (θ in K) were obtained: $C = 0.345$ and $\theta = -33.3$ for α-III; $C = 0.356$ and $\theta = -40.6$ for β-III. The effective moments (μ_{eff}) per formula were 1.66 μ_B for α-III and 1.69 μ_B for β-III, corresponding to a d^1 system.

Figure S4. Crystal photos showing the oxidation of α-III, as indicated by colour: a cluster of crystals exhibit darkening from the fringe of the blue colour (yellow circle).

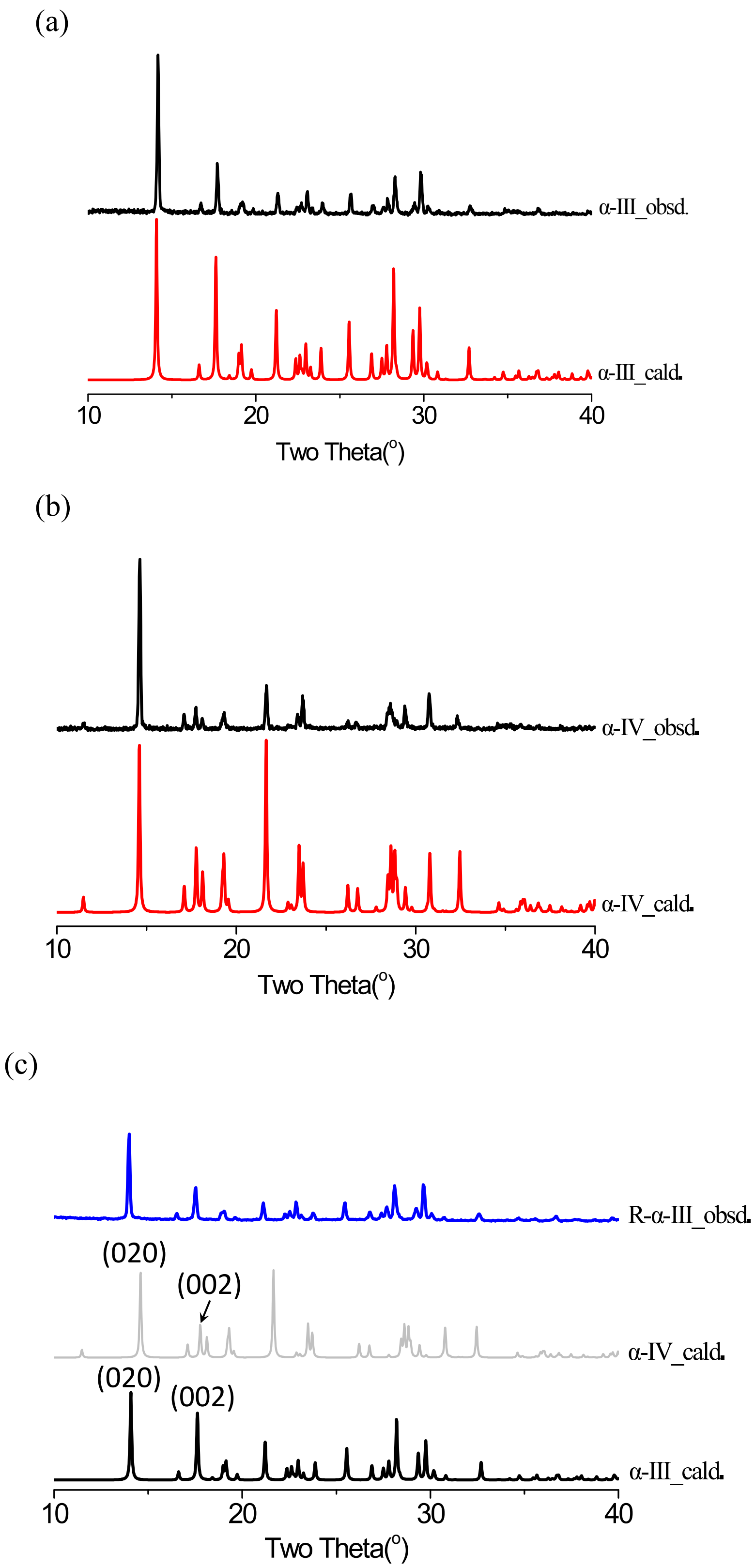

Figure S5. PXRD patterns (λ = 1.5418 Å) for (a) α-III, (b) α-IV and (c) the photo-reduced sample, R-α-III. Two reflection peaks, (020) and (002), in the calculated patterns of α-III and α-IV are labelled to show the variations in d-spacing (two theta) and intensities due to transformation between the Ti^{III} and Ti^{IV} structures.

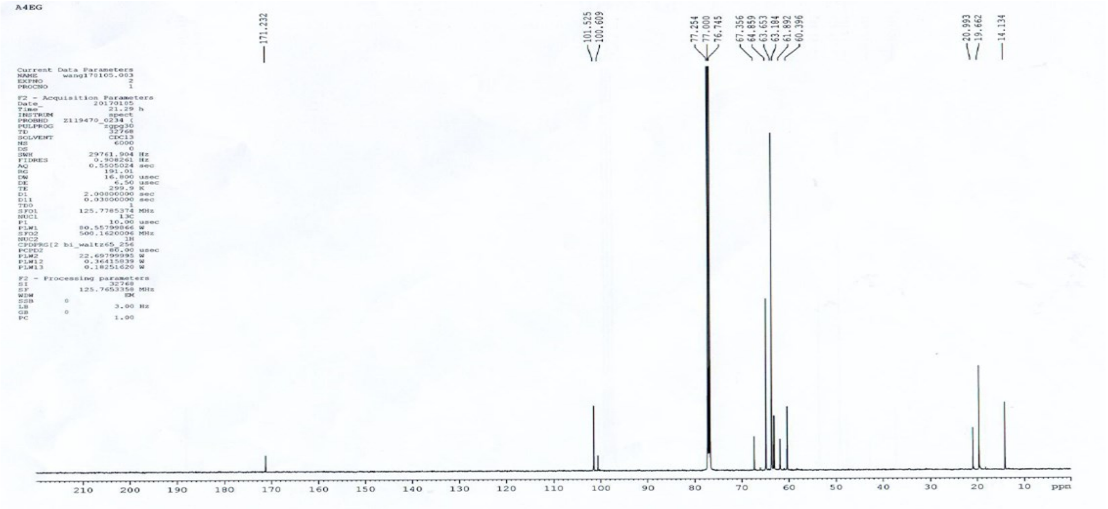

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Figure S6. Solution ^{13}C NMR spectrum of the filtrate after photoreduction of α-IV to α-III. The chemical shift at 171 ppm corresponds to C=O (red arrow), indicating that ethylene glycol was oxidised to provide e^-/H^+ for the photoreduction of α-IV to α-III.

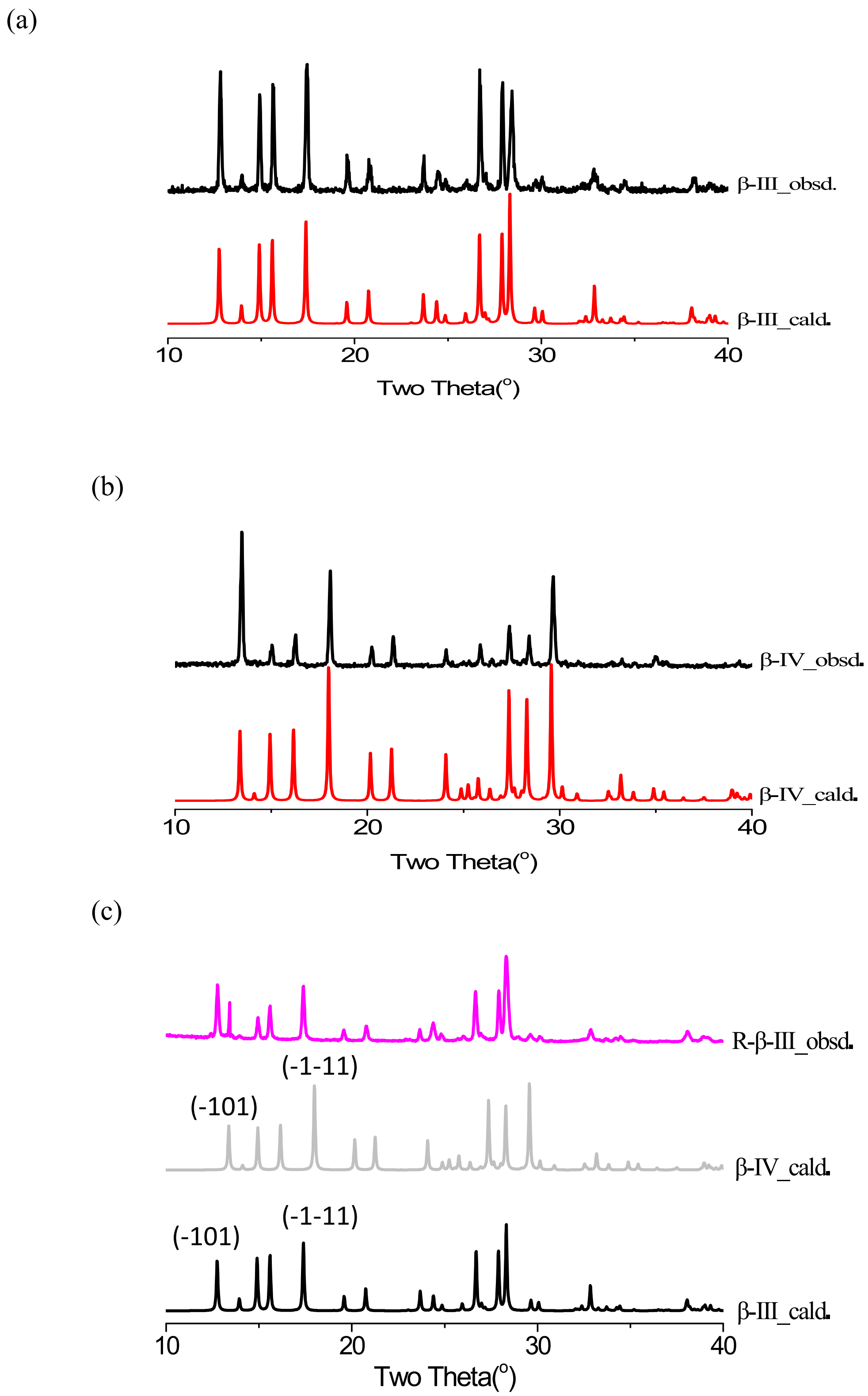

Figure S7. PXRD patterns (λ = 1.5418 Å) for (a) β-III, (b) β-IV and (c) the photo-reduced sample, R-β-III. Two reflection peaks, (-101) and (-1-11), in the calculated patterns of β-III and β-IV are labelled to show the variations in d-spacing (two theta) and intensities. The pattern of R-β-III has peaks for both β-III and β-IV structures, indicating that the transformation of β-IV back into β-III was incomplete.