Electronic Supplementary Material for PCCP
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Detection and kinetics of the single-crystal to single-crystal complete transformation of a thiiranium ion into thietanium ion

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Supplementary Information

1. Full Experimental Section.
2. Graphs of the cell parameters vs *t* for crystals B and C.
3 . Table with temporal evolution at RT of the cell parameters of samples A, B and C.

1. Full Experimental Section

Aged crystal A: approximate sphere of radius 0.2 mm. Data collection (SP) within 2θ=45°. 10978 reflections measured, 1938 unique. All non-H atoms anisotropic, except for the F atoms of the minor components of the disordered BF_4^- group. H atoms at calculated positions. 193 refined parameters. R1=0.086 for 1111 reflections with I>2σ(I), wR2=0.216 and gof=1.173 for all 1938 data.

Crystal B: prism of dimensions 0.32×0.25×0.04 mm. In spite of its small size, crystal B was chosen as the best one among the very few apparently single crystals of the batch. Unit-cell dimensions before/after data collection (SP) of set B1: *a*=13.643(2)/13.609(3) Å; *b*=11.668(2) /11.642(3) Å; *c*=18.844(5)/18.954(6) Å; *V*=2999.7(9)/3003(1) $Å^3$. Time elapsed between the two cell determinations: 6 days; time of exposure to X-rays: 118 h. 7343 reflections measured within 2θ=40°, table 1396 unique.

Disordered BF_4^- anion treated as in the aged crystal A; superposition of **1** and **2** for the cation, with five C atoms in common treated as anisotropic, all other cation atoms isotropic. 191 refined parameters.

R1=0.094 for 430 reflections with I>2σ(I), wR2=0.205 and gof=0.993 for all 1396 data. Site occupancy factor for **1**: 0.70(3). Unit-cell dimensions before/after data collection (SP) of set B2: *a*=13.562(3)/13.564(3) Å; *b*=11.475(3) /11.473(3) Å; *c*=19.170(6)/19.194(8) Å; *V*=2983(2)/2987(2) Å^3. Time elapsed between the two cell determinations: 7 days; time of exposure to X-rays: 109 h. 9754 reflections measured within 2θ=40°, 1383 unique. Both anion and cation treated as in the previous set B1 (same 191 refined parameters). R1=0.096 for 412 reflections with I>2σ(I), wR2=0.240 and gof=0.933 for all 1383 data. Site occupancy factor for **1**: 0.33(3). Unit-cell dimensions for data collection (BSA) of set B3 : *a*=13.550(4) Å; *b*=11.403(3) Å; *c*=19.242(6) Å; *V*=2973(2) Å^3. 51068 reflections measured within 2θ=40°, of which only 12798 with I>3σ(I), 1383 unique. Model for least-squares refinement as in the aged crystal A (disordered BF_4^- anion and pure thietanium ion **2**). R1=0.070 for 615 reflections with I>2σ(I), wR2=0.187 and gof=1.257 for all 1383 data.

Crystal C: prism of dimensions0.32×0.25×0.15 mm. The sample was kept at room temperature for 7 days before the first data collection started. Unit-cell dimensions before/after data collection (SP) of set C1: *a*=13.722(3)/13.686(4)Å; *b*=11.705(6)/11.698(6)Å; *c*=18.606(7)/18.709(8)Å; *V*=2988(2)/2995(2)Å^3. Time elapsed between the two cell determinations: 3 days; time of exposure to X-rays: 67 h. Data collection discontinued because of technical problems after the measurement of 4976 reflections with 2θ=40°, 1385 unique. Structure refined with **1** and BF_4^- atoms only (no disorder). All 17 non-H atoms anisotropic, H atoms at calculated positions. 161 refined parameters. R1=0.106 for 479 reflections with I>2σ(I), wR2=0.290 and gof=0.994 for all 1385 data. Unit-cell dimensions before/after data collection (SP) of set C2: *a*=13.566(4)/13.556(4)Å; *b*=11.508(6)/11.493(5)Å; *c*=19.152(8)/19.161(6)Å; *V*=2990(2)/2985(2)Å^3. Time elapsed between the two cell determinations: 6 days; time of exposure to X-rays: 132 h. 8785 reflections measured within 2θ=40°, 1389 unique. Structure refined with the same model of sets B1 and B2 (191 refined parameters). R1=0.097 for 663 reflections with I>2σ(I), wR2=0.281 and gof=1.020 for all 1389 data. Site occupancy factor for **1**: 0.30(2). Unit-cell dimensions for data collection (BSA) of set C3 : *a*=13.547(4) Å; *b*=11.406(4) Å; *c*=19.256(7) Å; *V*=2975(2) Å^3. 28462 reflections measured within 2θ=40°, 1384 unique. Model for least-squares refinement as in the aged crystal A and in set B3 (193 refined parameters). R1=0.074 for 658 reflections with I>2σ(I), wR2=0.111 and gof=0.901 for all 1384 data. Unit-cell dimensions for data collection (SP) of set C4 (no significant variation was detected between before and after the data collection) : *a*=13.552(4) Å; *b*=11.396(5) Å; *c*=19.273(8) Å; *V*=2965(2) Å^3. 10206 reflections measured within 2θ=40°, 1385 unique. Model for least-squares refinement as in set B3. R1=0.086 for 720 reflections with I>2σ(I), wR2=0.223 and gof=1.066 for all 1385 data.

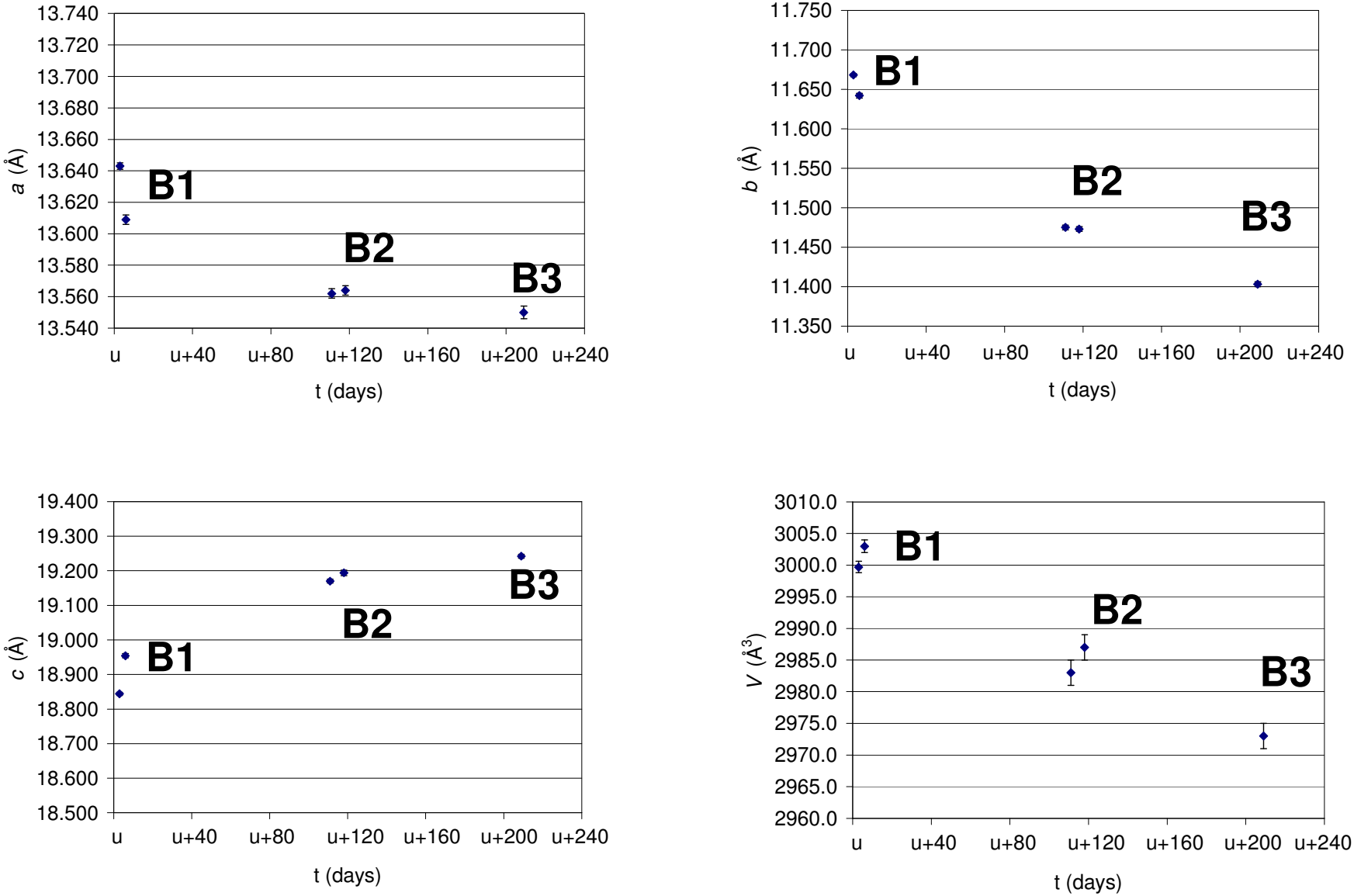
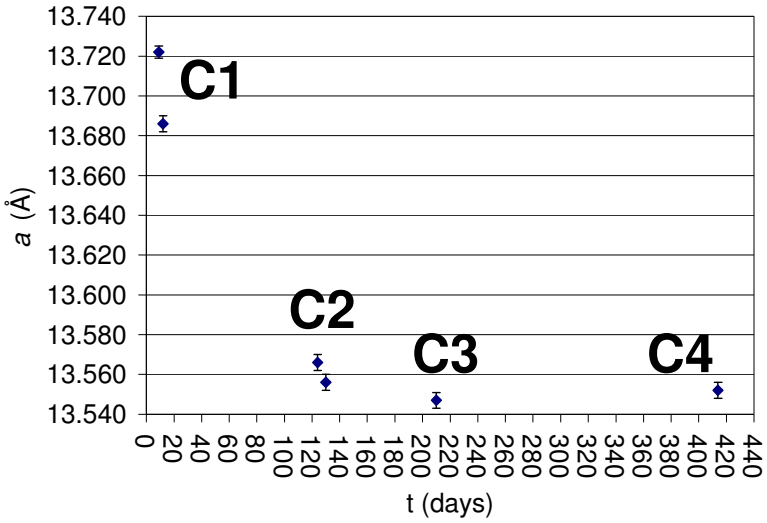
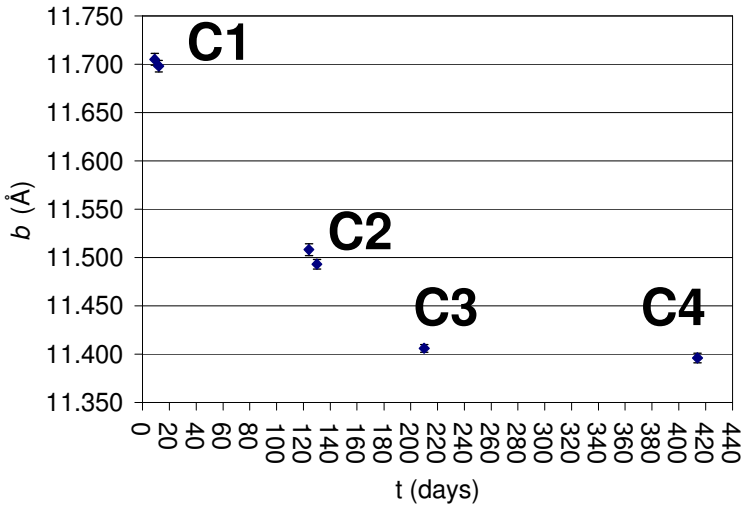
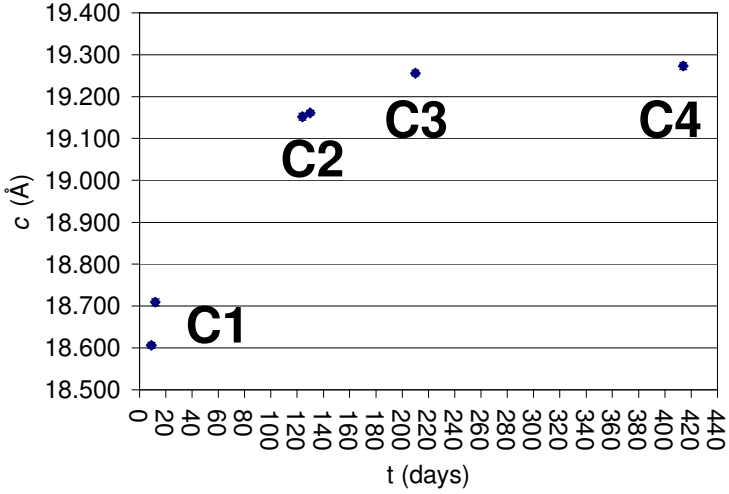


Figure S1. Crystal B: cell parameters (*a*, *b*, *c*, and *V*) as a function of the time the crystal had been kept at room temperature (the symbol "u" stands for "unknown time"). The labels in the graphs refer to the data sets.







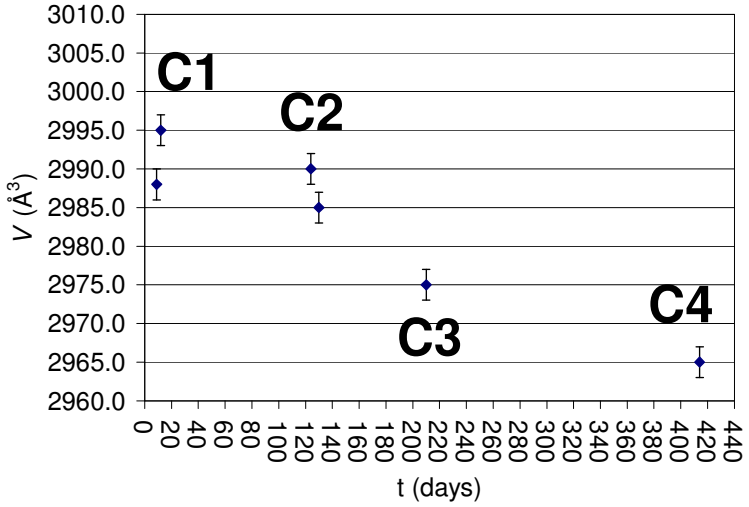


Figure S2. Crystal C: cell parameters (*a*, *b*, *c*, and *V*) as a function of the time the crystal had been kept at room temperature. The labels in the graphs refer to the data sets

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Table S1. Temporal evolution at room temperature of the unit-cell parameters of samples A, B and C (see text).

Sample	Data set	Time at RT [d]	X-ray exposure [h]	*a* [Å]	*b* [Å]	*c* [Å]	*V* [Å^3]	sof of **1**	Observed cation type
A	1	2	1	13.817(2)	11.703(2)	18.414(2)	2977.3(7)	1.0	**1**
		4	45	13.792(2)	11.704(1)	18.472(2)	2981.8(7)		
	2	6	86	13.768(2)	11.701(1)	18.533(2)	2985.8(7)		
		7	100	13.748(2)	11.699(2)	18.583(2)	2989.9(7)		
	aged	>1200	200	13.559(5)	11.370(5)	19.264(8)	2970(2)	0.0	**2**
B	1	Unknown (u)	1	13.643(2)	11.668(2)	18.844(5)	2999.7(9)	0.70(3)	Mixture of **1** and **2**
		u + 6	118	13.609(3)	11.642(3)	18.954(6)	3003(1)		
	2	u + 111	119	13.562(3)	11.475(3)	19.170(6)	2983(2)	0.33(3)	Mixture of **1** and **2**
		u + 118	227	13.564(3)	11.473(3)	19.194(8)	2987(2)		
	3	u + 209	228	13.550(4)	11.403(3)	19.242(6)	2973(2)	< 0.05	**2**
C	1	9	1	13.722(3)	11.705(6)	18.606(7)	2988(2)	≥ 0.95	**1**
		12	67	13.686(4)	11.698(6)	18.709(8)	2995(2)		
	2	124	68	13.566(4)	11.508(6)	19.152(8)	2990(2)	0.30(2)	Mixture of **1** and **2**
		130	199	13.556(4)	11.493(5)	19.161(6)	2985(2)		
	3	210	223	13.547(4)	11.406(4)	19.256(7)	2975(2)	~0.05	Mixture of **1** and **2**
	4	414	247	13.552(4)	11.396(5)	19.273(8)	2965(2)	~0.0	**2**