Supporting Information for

Formation of intermetallic PdIn nanoparticles: Influence of surfactants on nanoparticle structure

Baiyu Wang[1], Jette K. Mathiesen[2], Andrea Kirsch[1], Nicolas Schlegel[3], Andy S. Anker[1], Frederik L. Johansen[1], Emil T.S. Kjær[1], Olivia Aalling-Frederiksen[1], Tobias M. Nielsen[1], Maria S. Thomsen[1], Rasmus K. Jakobsen[1], Matthias Arenz[3], Kirsten M.Ø. Jensen*[1]

1) Department of Chemistry, University of Copenhagen, Universitetsparken 5, 2100 Copenhagen Ø, Denmark
2) Department of Physics, Technical University of Denmark, Fysikvej, 2800 Kongens Lyngby, Denmark
3) Department of Chemistry, Biochemistry and Pharmaceutical Sciences, University of Bern, Freiestrasse 3, 3012 Bern, Switzerland
*Corresponding author: kirsten@chem.ku.dk

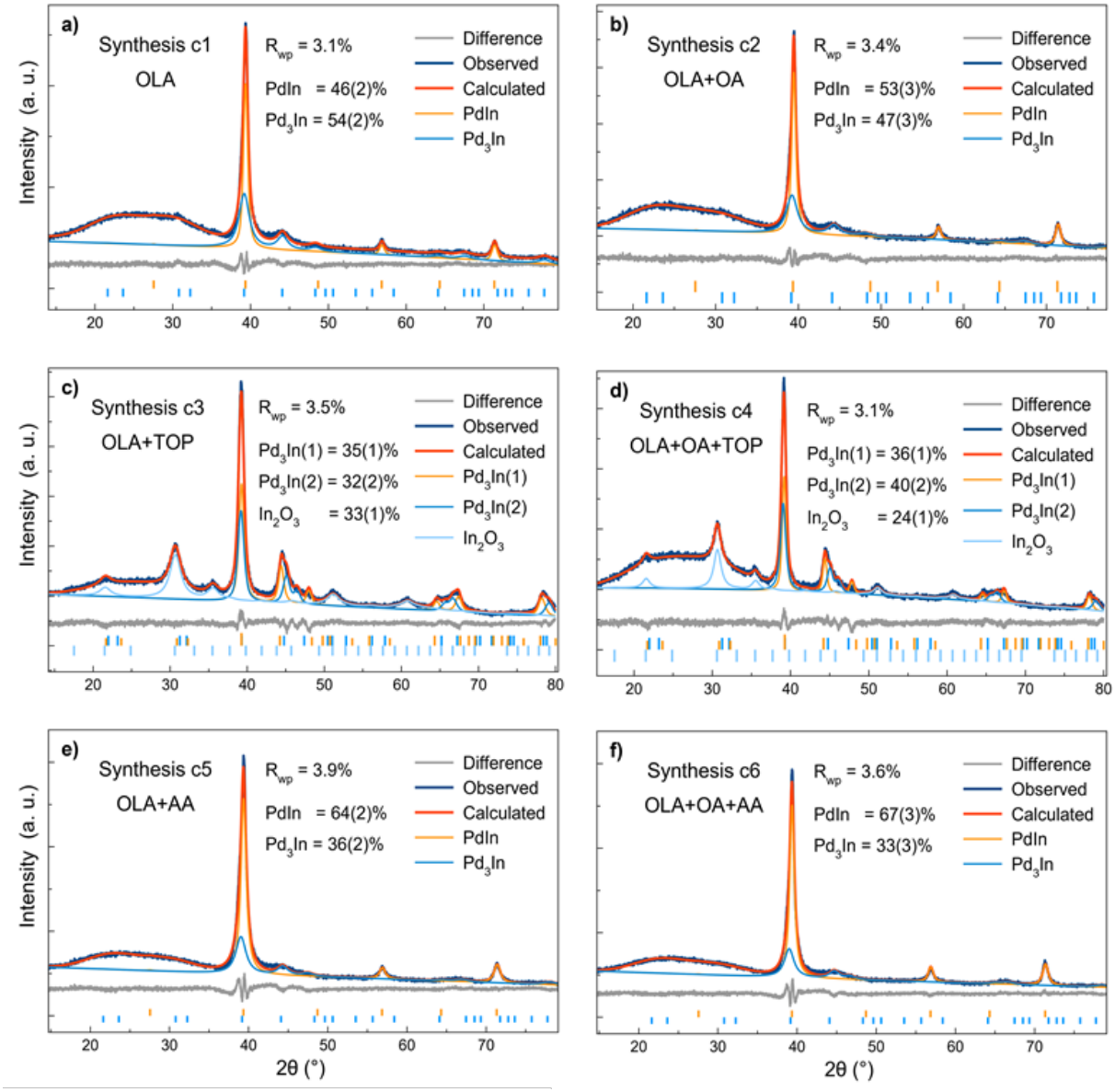

Figure S1a. Rietveld refinements of PXRD patterns obtained from syntheses **c1-c6** (a-f).

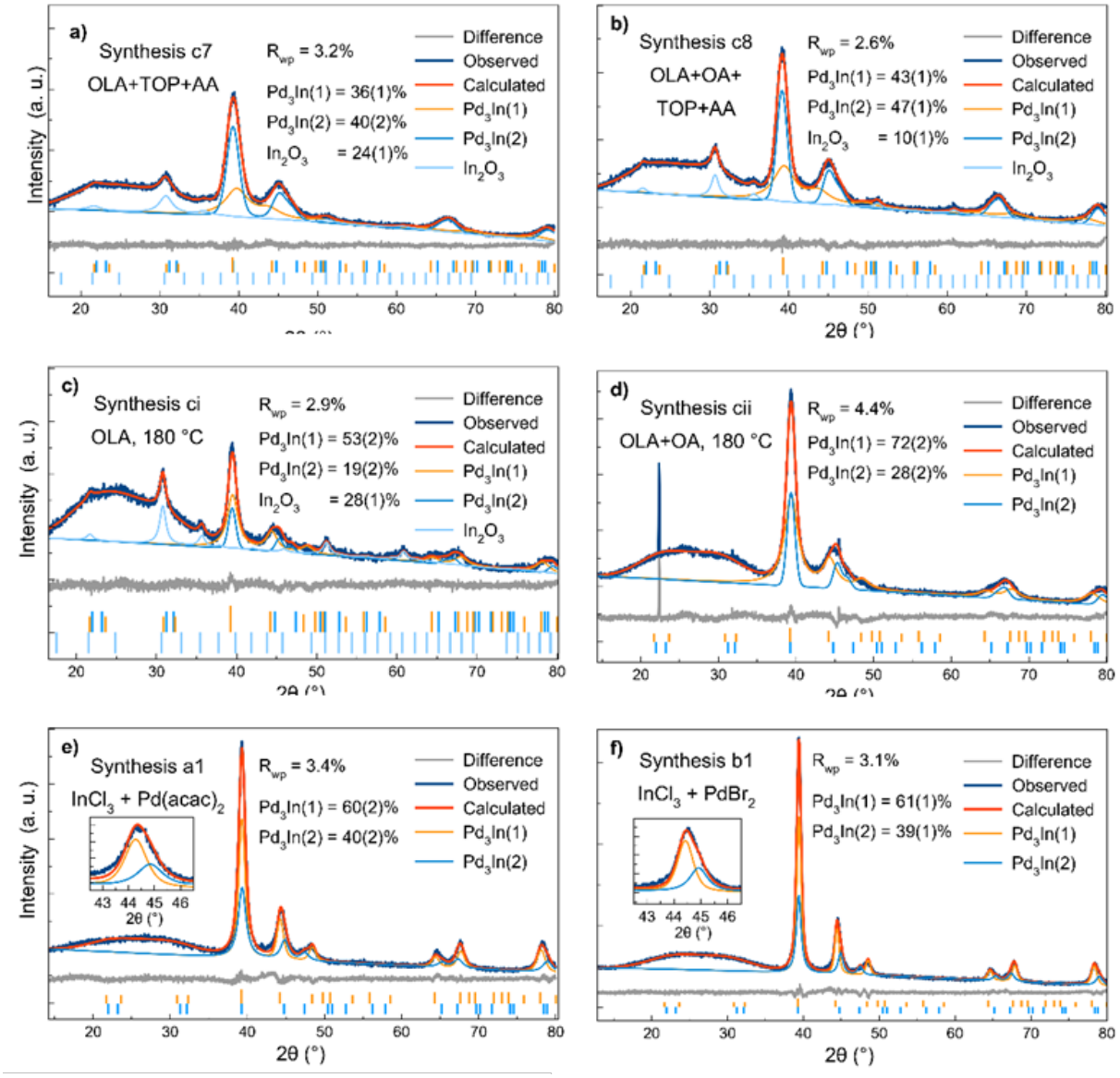

Figure S1b. Rietveld refinements of PXRD patterns obtained from syntheses a) **c7,** b) **c8**, c) **ci**, d) **cii**, e) **a1** and f) **b1**.

Table S1. Parameters obtained from Rietveld refinements.

		PdIn			Pd_3In[a]				In_2O_3		
Sample	Rwp /%	Frac /%	a /Å	Size /nm	Frac /%	a /Å	c /Å	Size /nm	Frac /%	a /Å	Size /nm
a1	3.4				60(2)	4.0929(8)	3.759(1)	7.0(3)			
					40(2)	4.044(2)	3.833(3)	5.1(3)			
b1	3.1				61(1)	4.0844(4)	3.7555(5)	10.8(3)			
					39(1)	4.0418(6)	3.833(1)	8.3(4)			
c1	3.1	46(2)	3.2363(5)	10.4(3)	54(2)	4.105(1)	3.764(3)	3.9(1)			
c2	3.4	53(3)	3.2386(5)	11.0(1)	47(3)	4.096(2)	3.795(3)	3.9(2)			
c3	3.5				35(1)	4.0839(6)	3.7947(8)	8.5(4)	33(1)	10.112(2)	3.5(2)
					32(1)	4.0257(7)	3.913(1)	7.2(3)			
c4	3.1				36(1)	4.0860(6)	3.8065(9)	12.4(5)	24(1)	10.116(3)	5.6(1)
					40(1)	4.0309(7)	3.941(1)	8.2(3)			
c5	3.9	64(2)	3.2346(5)	8.0(1)	36(2)	4.086(2)	3.828(4)	4.0(2)			
c6	3.6	67(3)	3.2369(4)	9.7(1)	33(3)	4.056(2)	3.895(3)	4.2(2)			
c7	2.9				44(2)	4.133(4)	3.623(7)	1.6(1)	12(1)	10.091(6)	3.0(1)
					44(2)	4.027(1)	3.893(2)	4.6(2)			
c8	2.6				43(1)	4.136(4)	3.671(6)	1.9(1)	10(1)	10.092(4)	5.4(2)
					47(1)	4.0260(9)	3.908(1)	5.5(2)			
ci	2.9				53(2)	4.094(2)	3.749(3)	3.9(1)	28(1)	10.119(3)	6.4(2)
					19(2)	4.016(2)	3.897(3)	8(1)			
cii	4.4				72(2)	4.091(2)	3.763(3)	3.0(1)			
					28(2)	4.009(2)	3.906(2)	7.6(8)			
PdIn [1]			3.246								
Pd_3In [2]						4.0729(1)	3.7918(2)				
In_2O_3 [3]										10.117(1)	

Errors are given in parentheses

[a]When two Pd_3In phases were fitted, the first row gives the values of $Pd_3In(1)$, while the second row gives $Pd_3In(2)$

[1] Literature data taken from the ICSD (59473), Savitskii, E.m.; Polyakova, V.P.; Urvachev, V.P., An investigation of the polythermal Pn In - Pd Sc cross-section. *Metally, Izvestiya Akademii Nauk SSSR* **1980**, 226-230.

[2] Literature data taken from the ICSD (59476), Harris, I.R.; Norman, M.; Bryant, A.W., A study of some palladium-indium, platinum-indium and platinum-tin alloys. *Journal of the Less-Common Metals* **1968**, *16* (4), 427-440

[3] Marezio, M., Refinement of the crystal structure of In2 O3 at two wavelengths. *Acta Cryst.* **1966**, *20*, 723-728

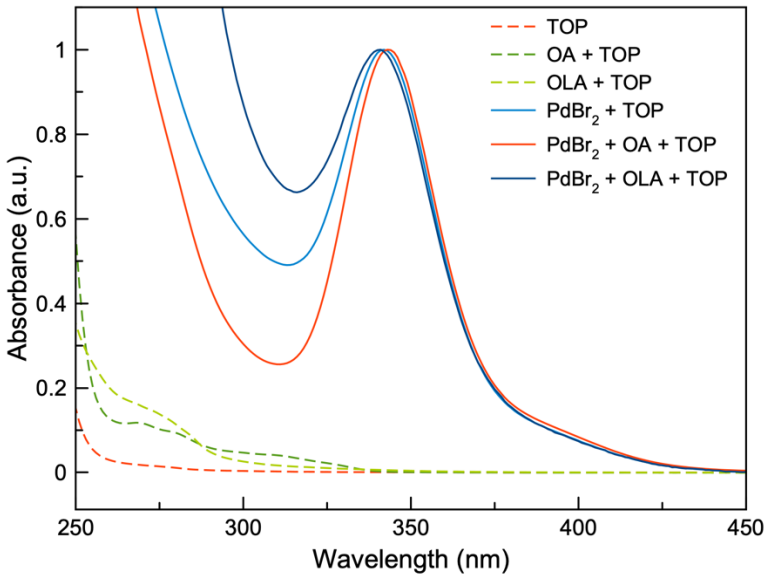

Figure S2. Absorption spectra of the metal precursor $PdBr_2$ with different additives, OA and TOP.

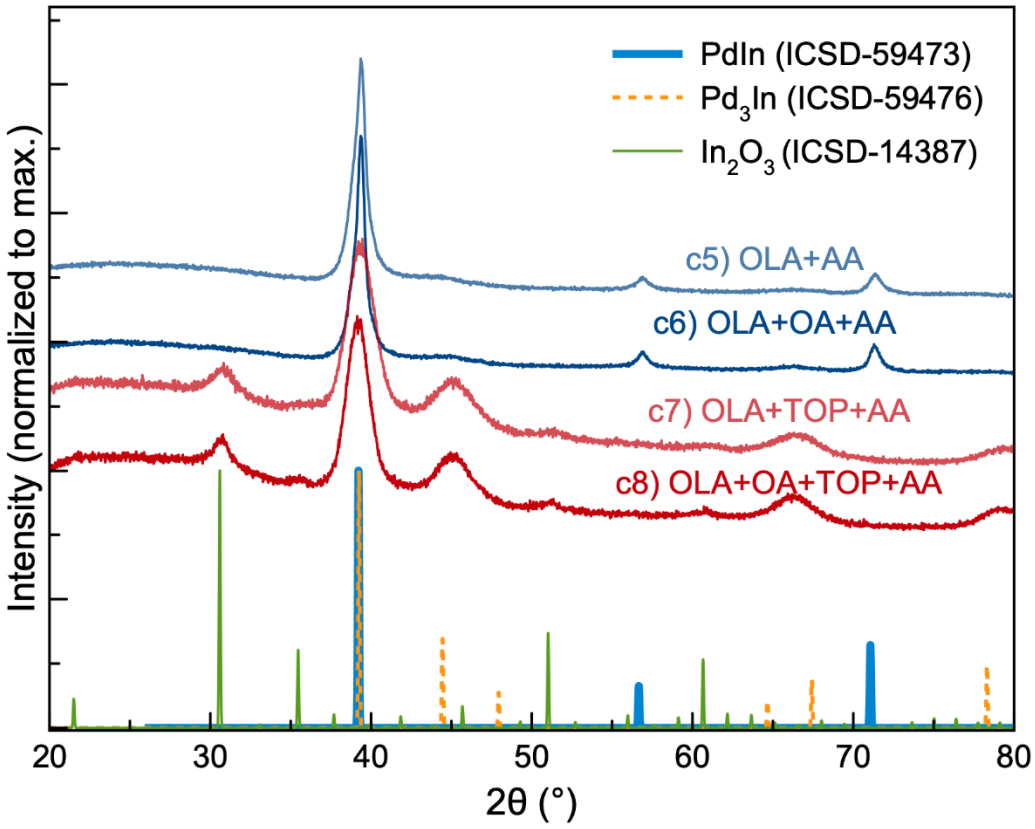

Figure S3. PXRD patterns of the products from syntheses **c5-c8**, containing different surfactants: c5) OLA+AA, c6) OLA+OA+AA, c7) OLA+TOP+AA, c8) OLA+OA+TOP+AA.

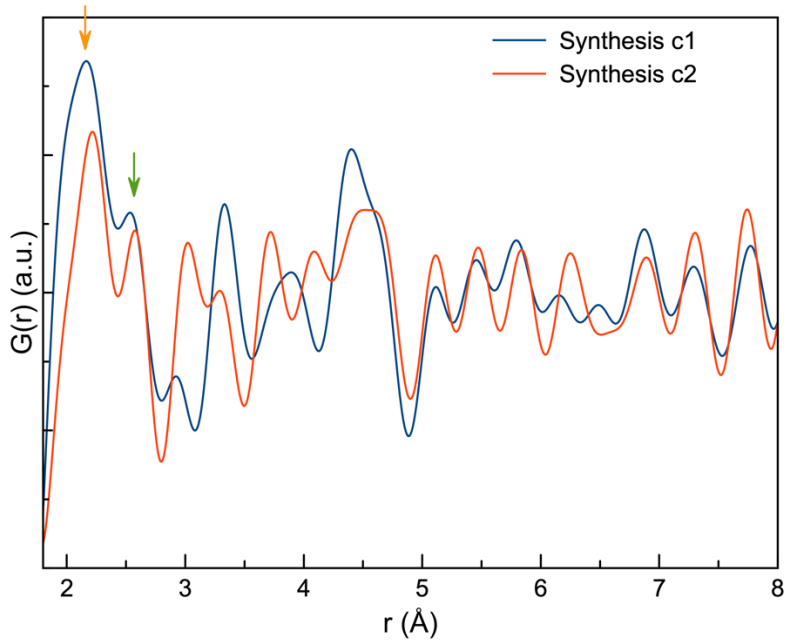

Figure S4. PDFs obtained from the PdIn-precursor solution at room temperature from syntheses **c1** and **c2**.

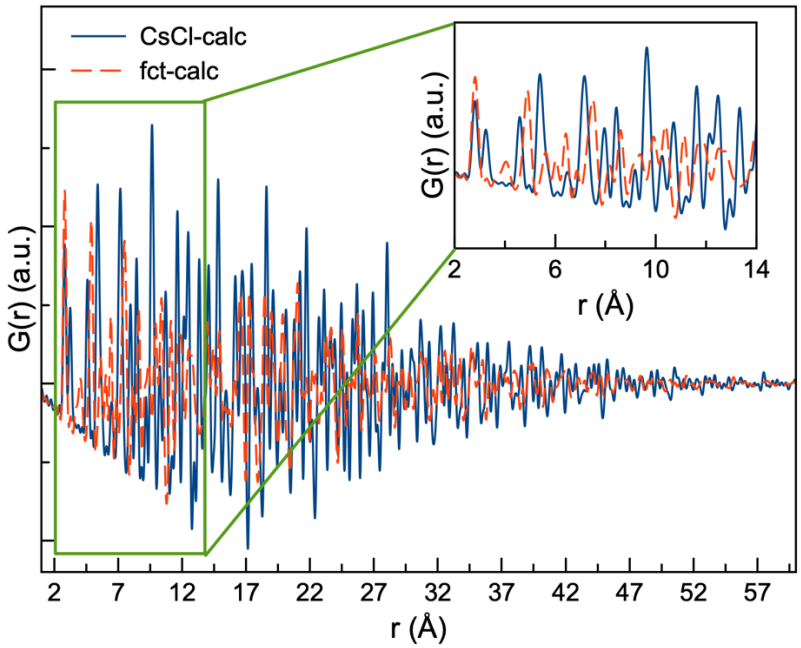

Figure S5. Calculated PDFs from PdIn (blue) and Pd_3In (red) model respectively.

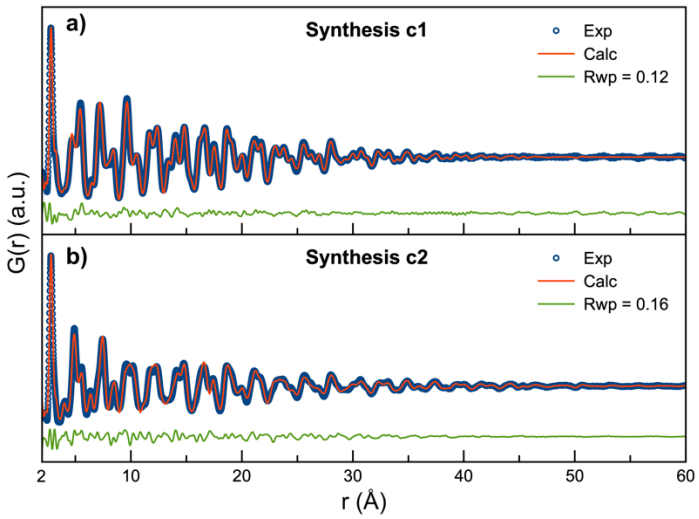

Figure S6. Real-space Rietveld refinement of PDFs from final product produced by a) synthesis **c1** and b) synthesis **c2**.

Table S2. Refined values obtained from PDF refinement of the last frame of PDFs from syntheses **c1** and **c2**.

	Synthesis **c1**	Synthesis **c2**
R_w	0.123	0.166
Phase fraction / % **(PdIn / Pd_3In)**	85 / 15	54 / 46
Scale factor **(PdIn / Pd_3In)**	0.845/ 0.599	0.261/ 0.427
SPdiameter / Å **(Pd_3In)**	39	36
Pd_3In cell / Å **(a / c)**	4.11 / 3.78	4.07/ 3.86
PdIn cell / Å	3.25	3.25
δ_2 /Å^2	4.5	4.3
U_{iso}(Pd) /Å^2 **(PdIn / Pd_3In)**	0.022 / 0.020	0.046 / 0.021
U_{iso}(In) /Å^2 **(PdIn / Pd_3In)**	0.030 / 0.079	0.061 / 0.021

For both samples, the parameters refined included scale factors, unit cell parameters, atomic displacement parameters (ADPs), spherical diameter (SPdiameter) and δ_2, which accounts for the correlated local atomic motion in the structure.

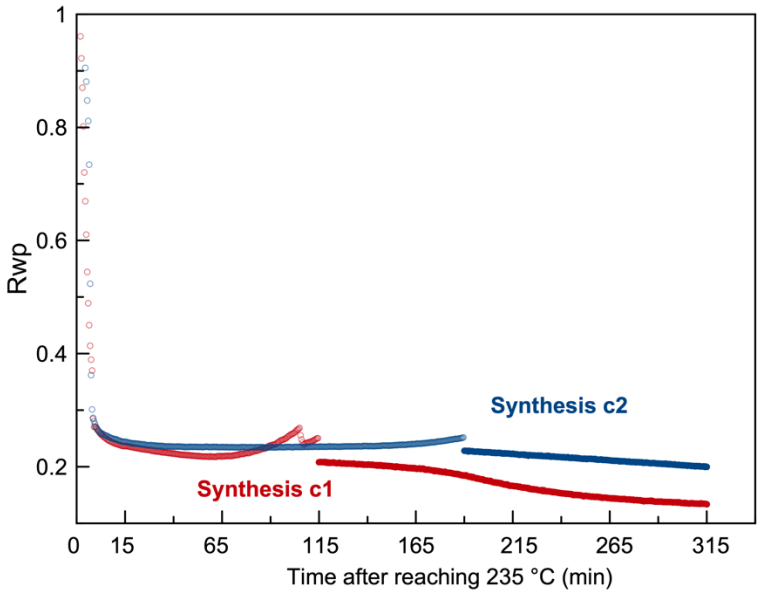

Figure S7. Rwp values from sequential refinements of PDFs from syntheses **c1** and **c2**, are shown in red and blue respectively. Rwp values from the single Pd_3In model are shown in hollow circles while Rwp values from the two-phase model are shown in filled dots.

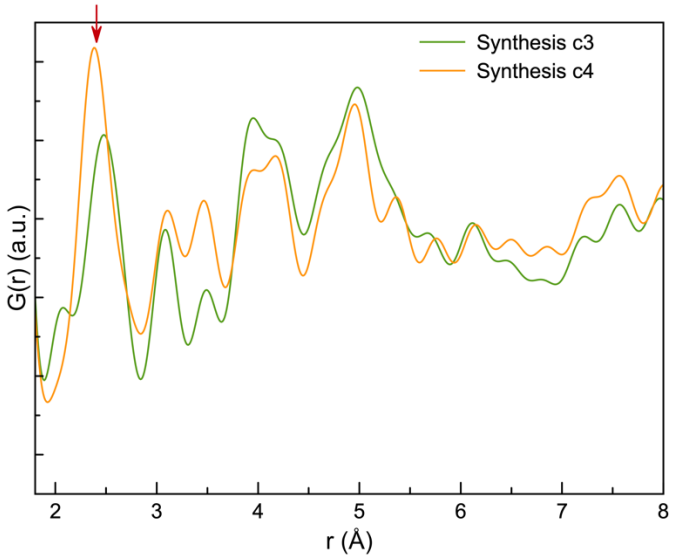

Figure S8: PDFs obtained from the PdIn-precursor solution at room temperature from syntheses **c3** and **c4**.

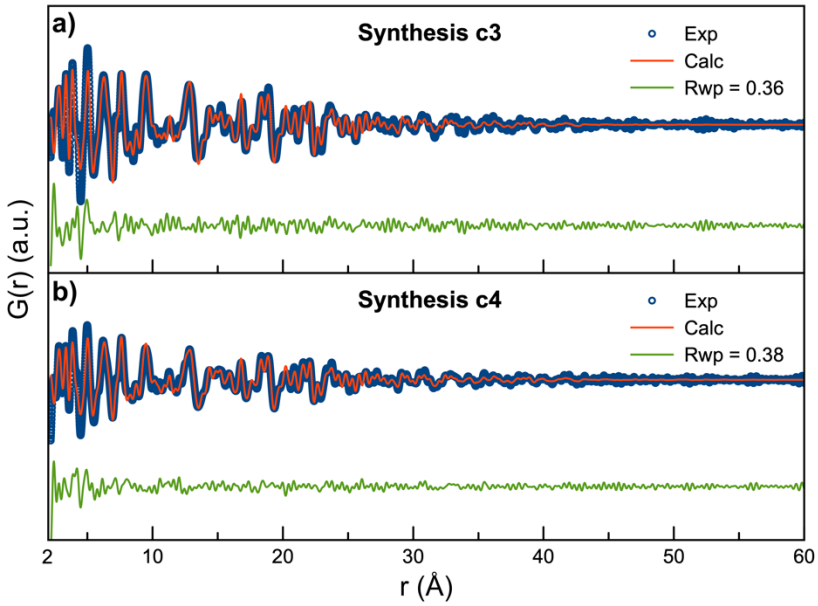

Figure S9. Real-space Rietveld refinement of PDFs from final product produced by a) synthesis **c3** and b) synthesis **c4**.

Table S3. Refined values obtained from PDF refinement of the last frame of PDFs from Syntheses **c3** and **c4**.

	Synthesis **c3**	Synthesis **c4**
R_w	0.358	0.378
Phase fraction / % **(PdIn / Pd_3In)**	93 / 7	93 / 7
Scale factor **(Pd_3In / In_2O_3)**	0.217/ 0.203	0.078/ 0.080
SPdiameter / Å **(Pd_3In / In_2O_3)**	33 / 64	34 / 75
Pd_3In cell / Å **(a / c)**	4.08 / 3.90	4.08/ 3.93
In_2O_3 cell / Å	10.14	10.14
δ_2 /Å^2	0.9	0.9
U_{iso}(Pd) /Å^2 **(Pd_3In)**	0.024	0.019
U_{iso}(In) /Å^2 **(Pd_3In / In_2O_3)**	0.024 / 0.008	0.019 / 0.009
U_{iso}(O) /Å^2 **(In_2O_3)**	0.008	0.009

For both samples, the parameters refined included scale factors, unit cell parameters, atomic displacement parameters (ADPs), spherical diameter (SPdiameter)and δ_2, which accounts for the correlated local atomic motion in the structure.

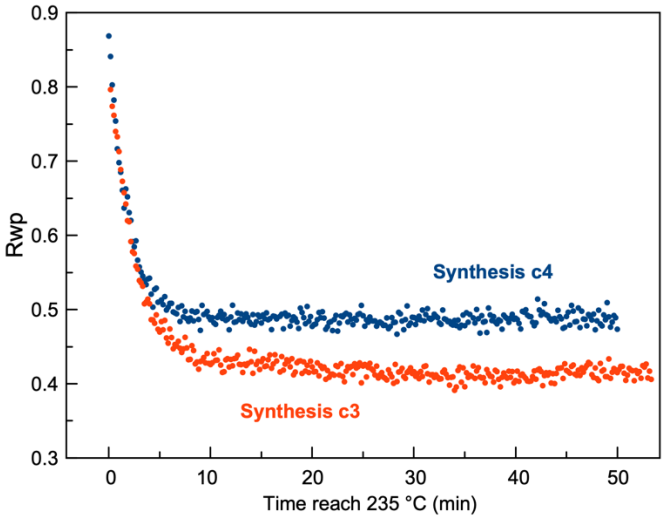

Figure S10. Rwp values from two-phase sequential refinements of PDFs from syntheses **3** and **4**, are shown in red and blue respectively.

References:

1. Coelho, A.A., *TOPAS and TOPAS-Academic: an optimization program integrating computer algebra and crystallographic objects written in C++.* Journal of Applied Crystallography, 2018. **51**(1): p. 210-218.