Supplementary Information: Temperature dependent local structure coherence of surface-modified $BaTiO_3$ nanocubes

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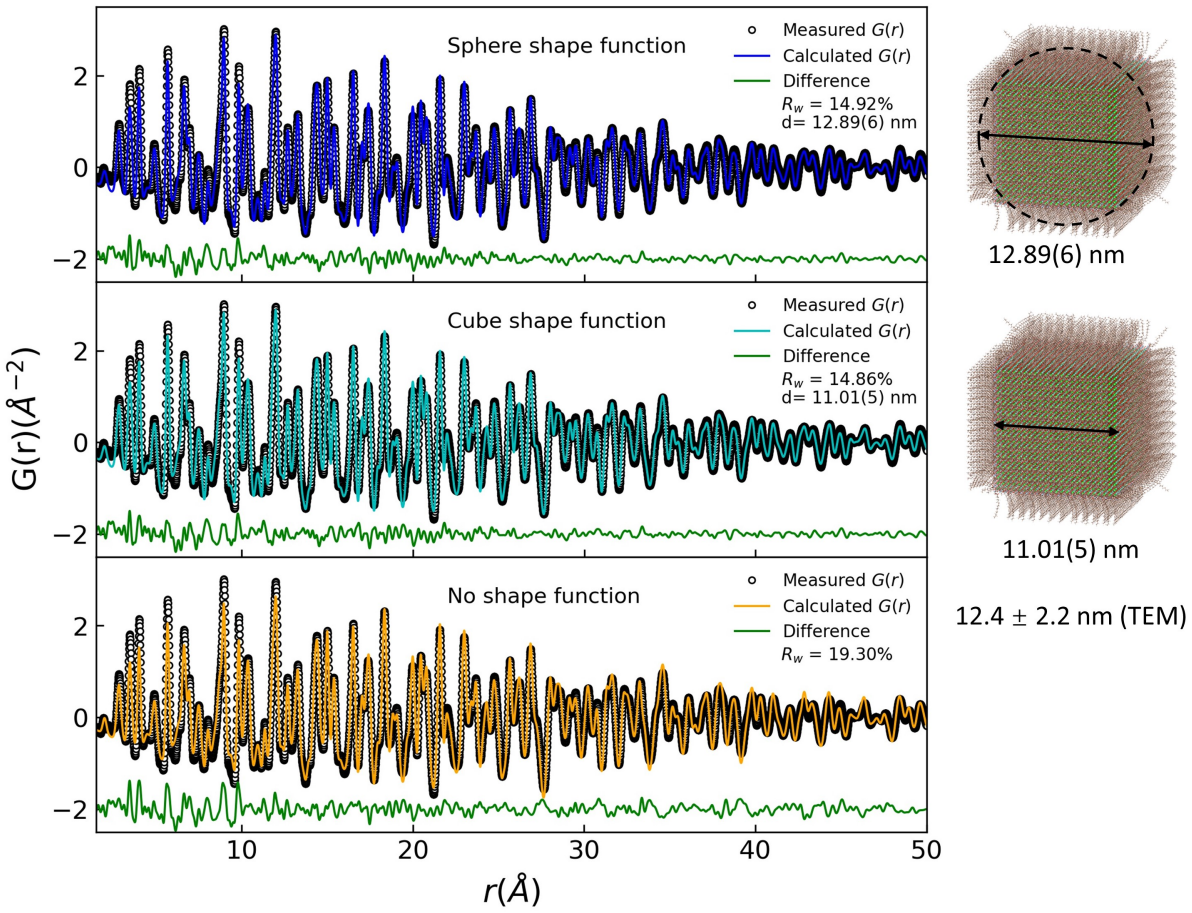

Figure S1: X-ray PDF fitting patterns of BTnc@OA for ∼12 nm nanocubes using a sphere shape function (top), cube shape function (middle) and no shape function (bottom). An improved fit residual and physically relevant coherent particle edge length were obtained by using the cube shape function (the obtained edge length of 11.01(5) nm is within range of the average TEM edge length of 12.4 ± 2.2 nm.

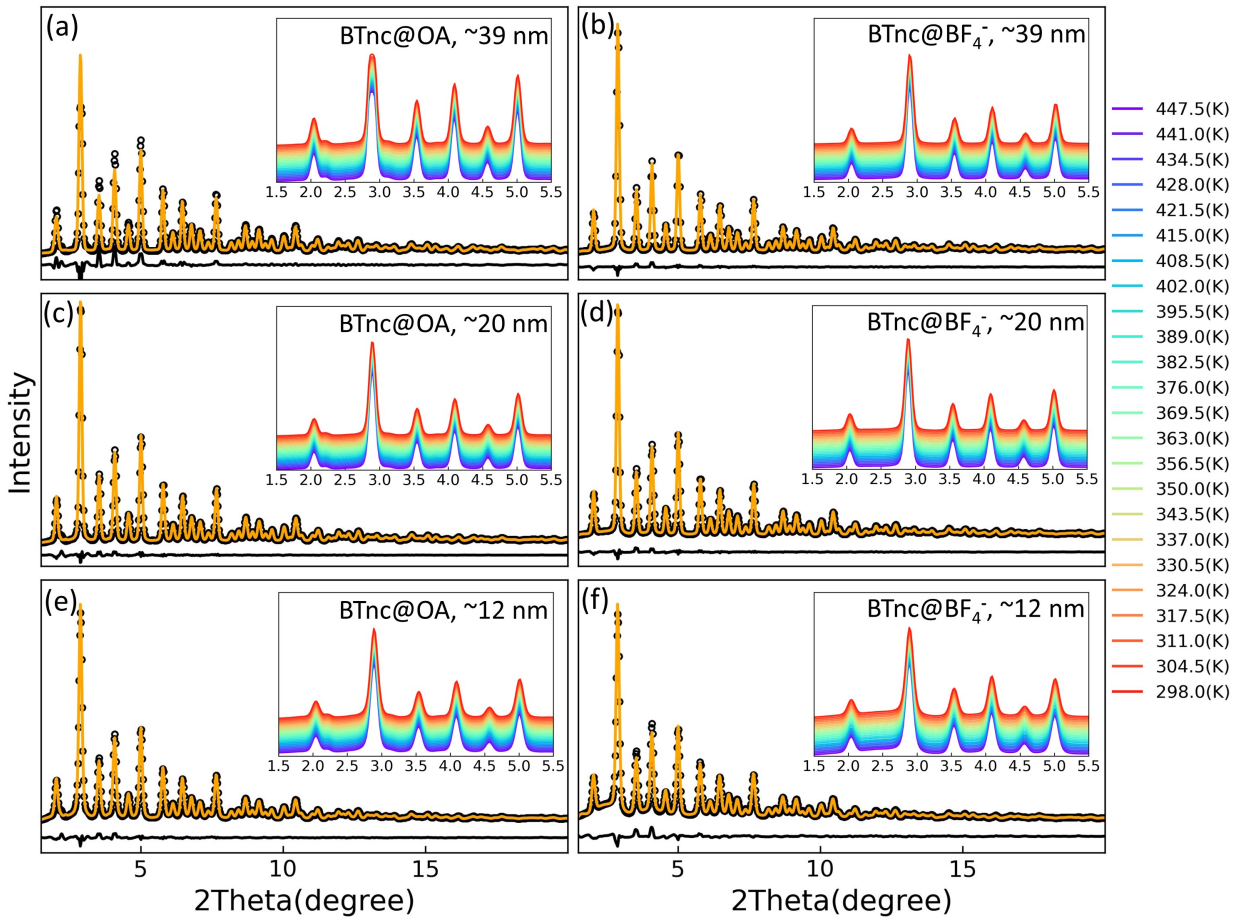

Figure S2: Rietveld refinements of synchrotron X-ray diffraction data of $BaTiO_3$ nanocubes to tetragonal $P4mm$ models, inserts show the temperature-dependent patterns from 300 K (Purple) to 440 K (Red). A mismatch in low 2θ peak intensities is noted in the Rietveld refinement result of the ∼39 nm BTnc@OA data in Figure S2(a), likely due to detector overexposure for the first several measurements in the series.

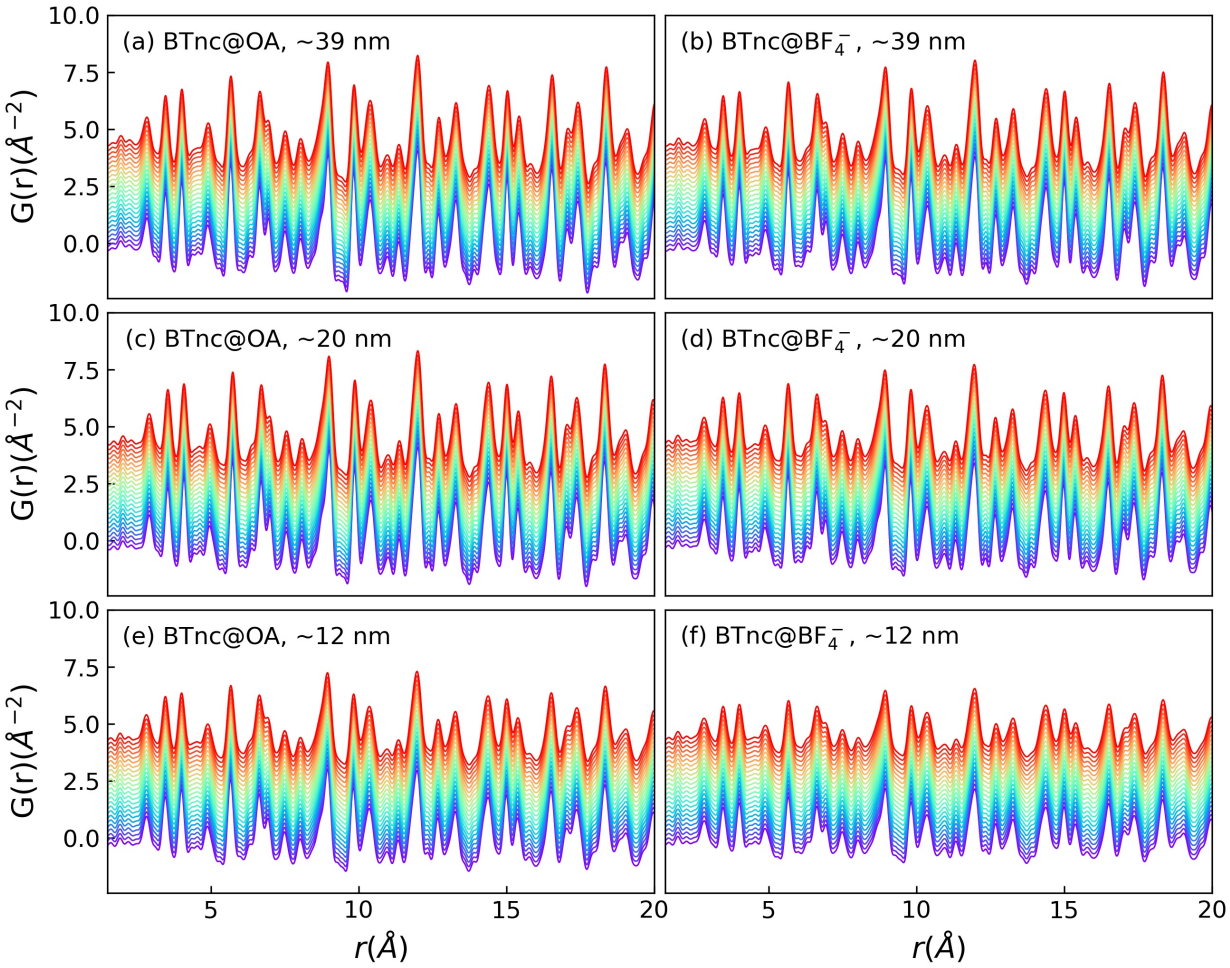

Figure S3: Synchrotron X-ray PDF patterns of $BaTiO_3$ nanocubes from 300 K (Purple) to 440 K (Red).

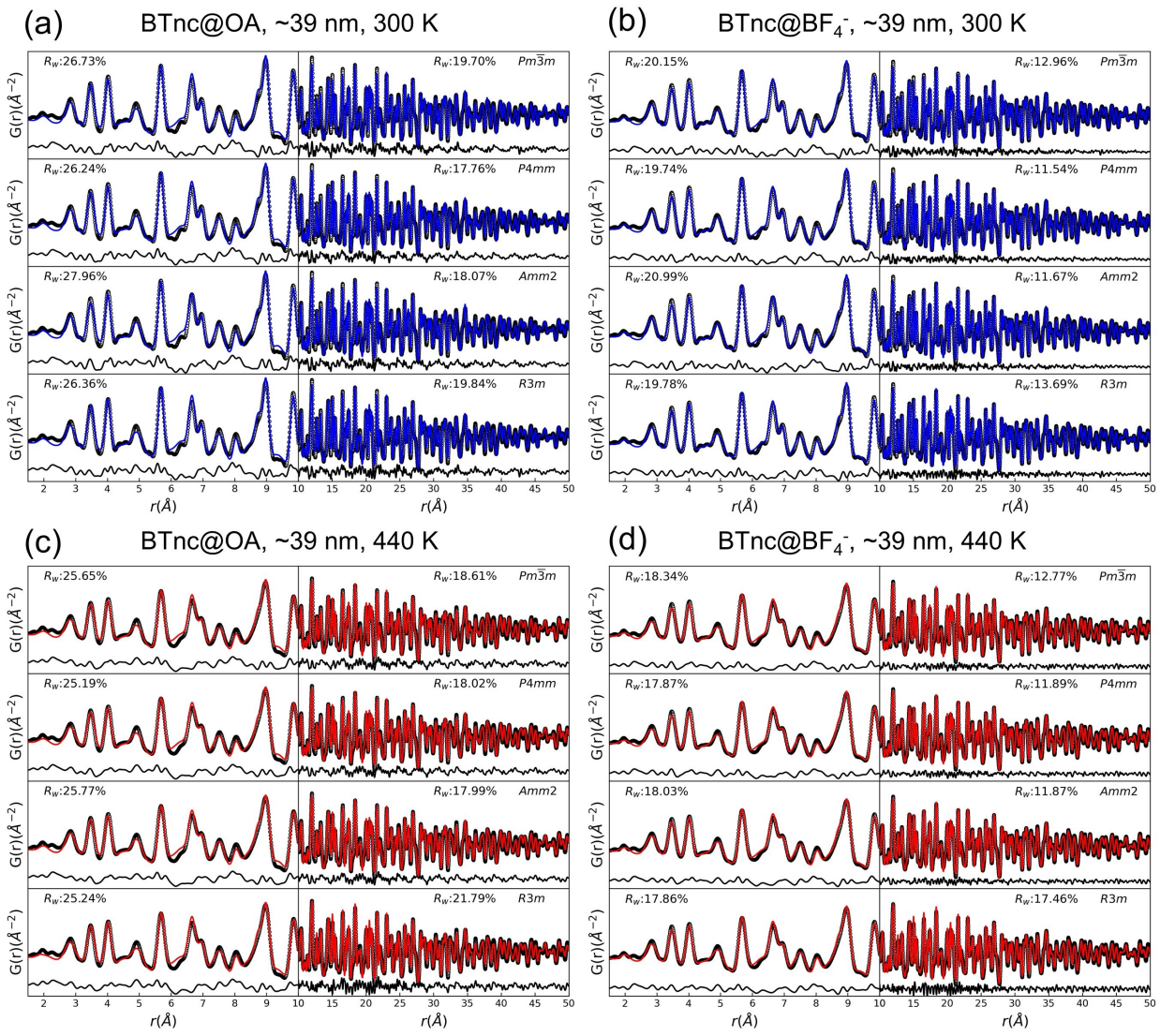

Figure S4: PDF refinements of synchrotron X-ray data using centrosymmmetric cubic $Pm\bar{3}m$, and non-centrosymmmetric (tetragonal $P4mm$, orthorhombic $Amm2$ and rhombohedra $R3m$) at (a, b) 300 K and (c, d) 440 K for $BaTiO_3$ ∼39 nm nanocubes with OA and BF_4 ligands capped.

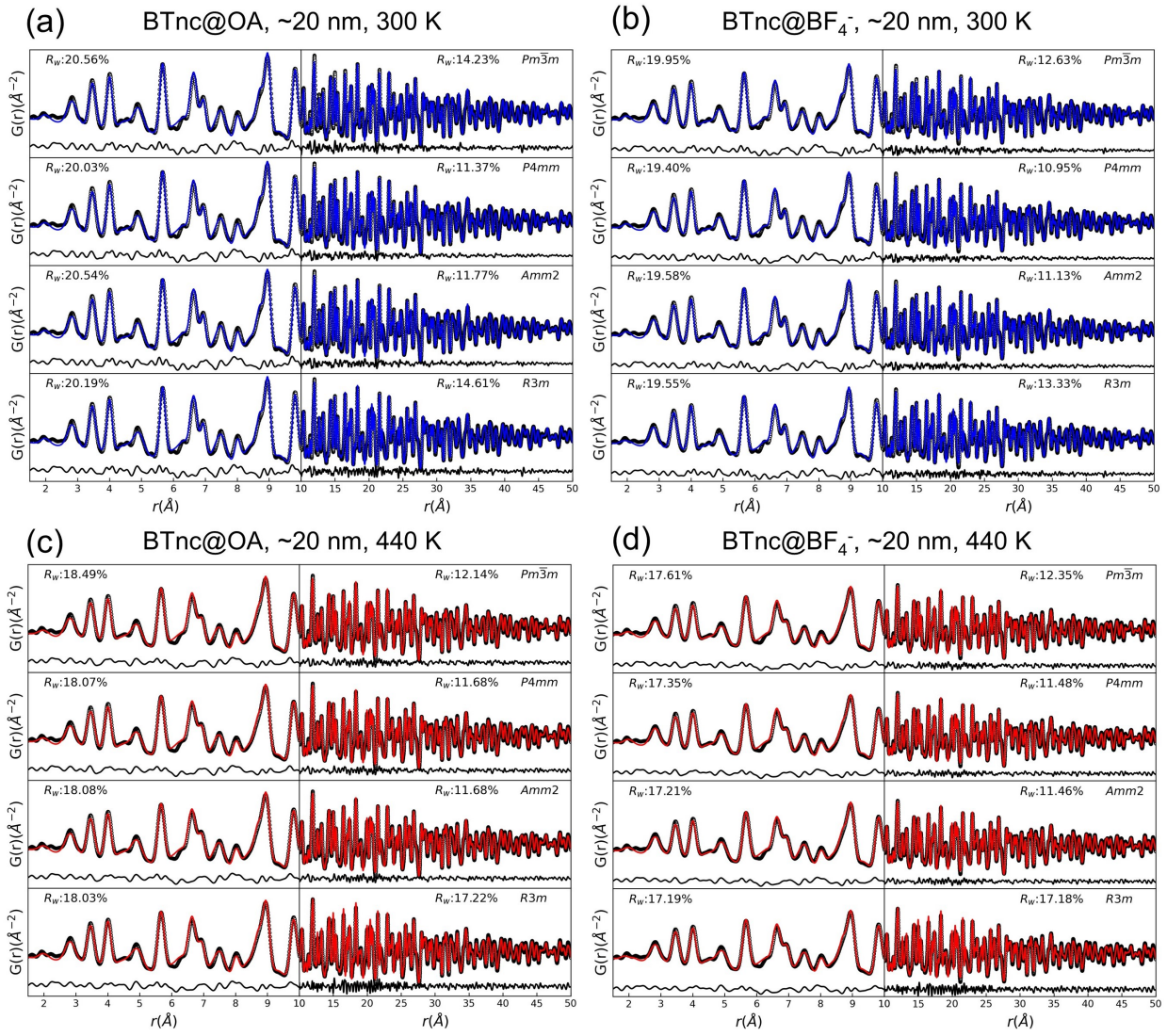

Figure S5: PDF refinements of synchrotron X-ray data using centrosymmmetric cubic $Pm\bar{3}m$, and non-centrosymmmetric (tetragonal $P4mm$, orthorhombic $Amm2$ and rhombohedra $R3m$) at (a, b) 300 K and (c, d) 440 K for $BaTiO_3$ ~20 nm nanocubes with OA and BF_4 ligands capped.

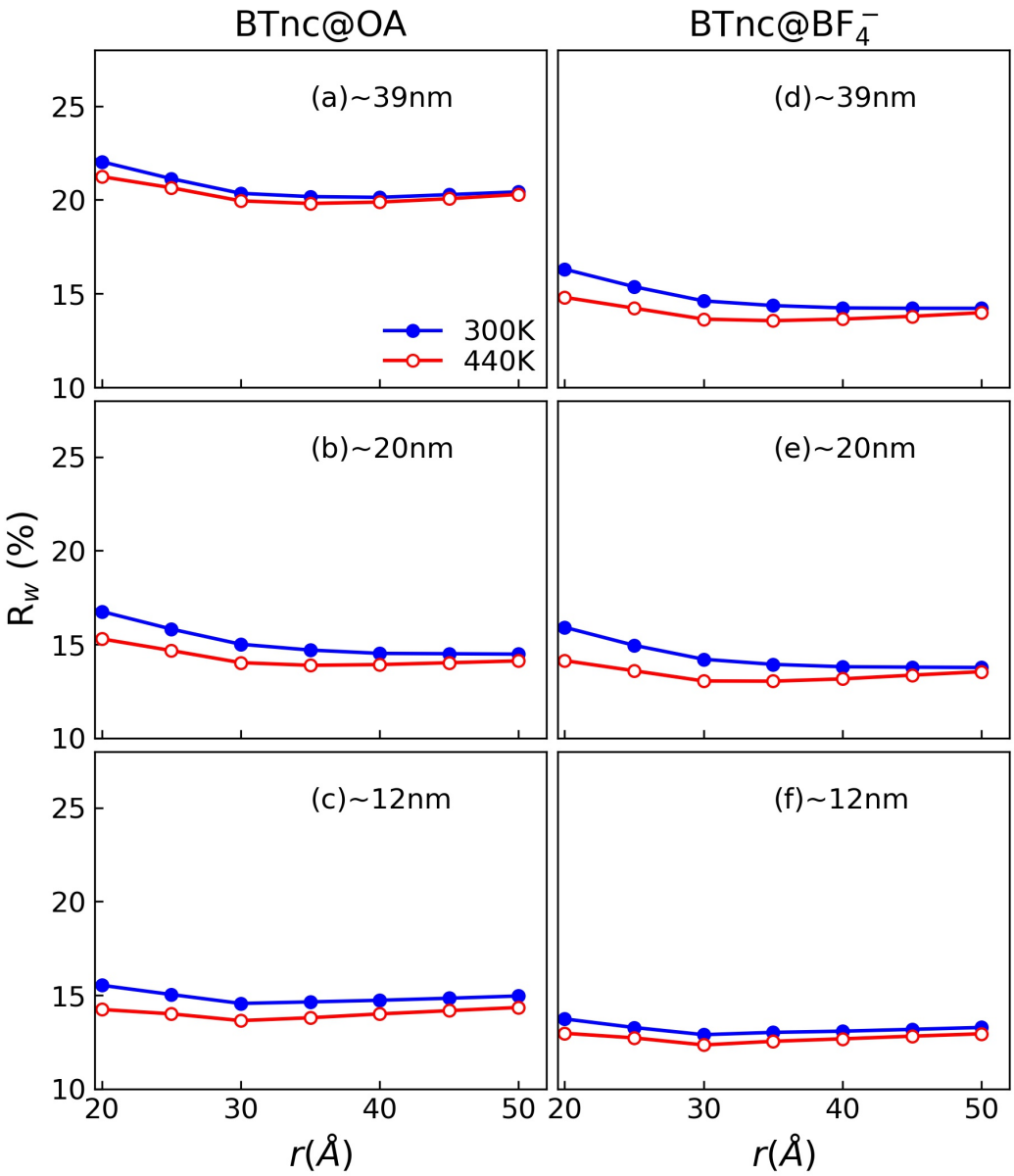

Figure S6: Goodness of fit (R_w) resulting from PDF refinements using non-centrosymmmetric tetragonal $P4mm$ model with varying r_{max} range from 20 Åto 50 Å. Blue symbols indicate 300 K data and red symbols indicate 440 K data.

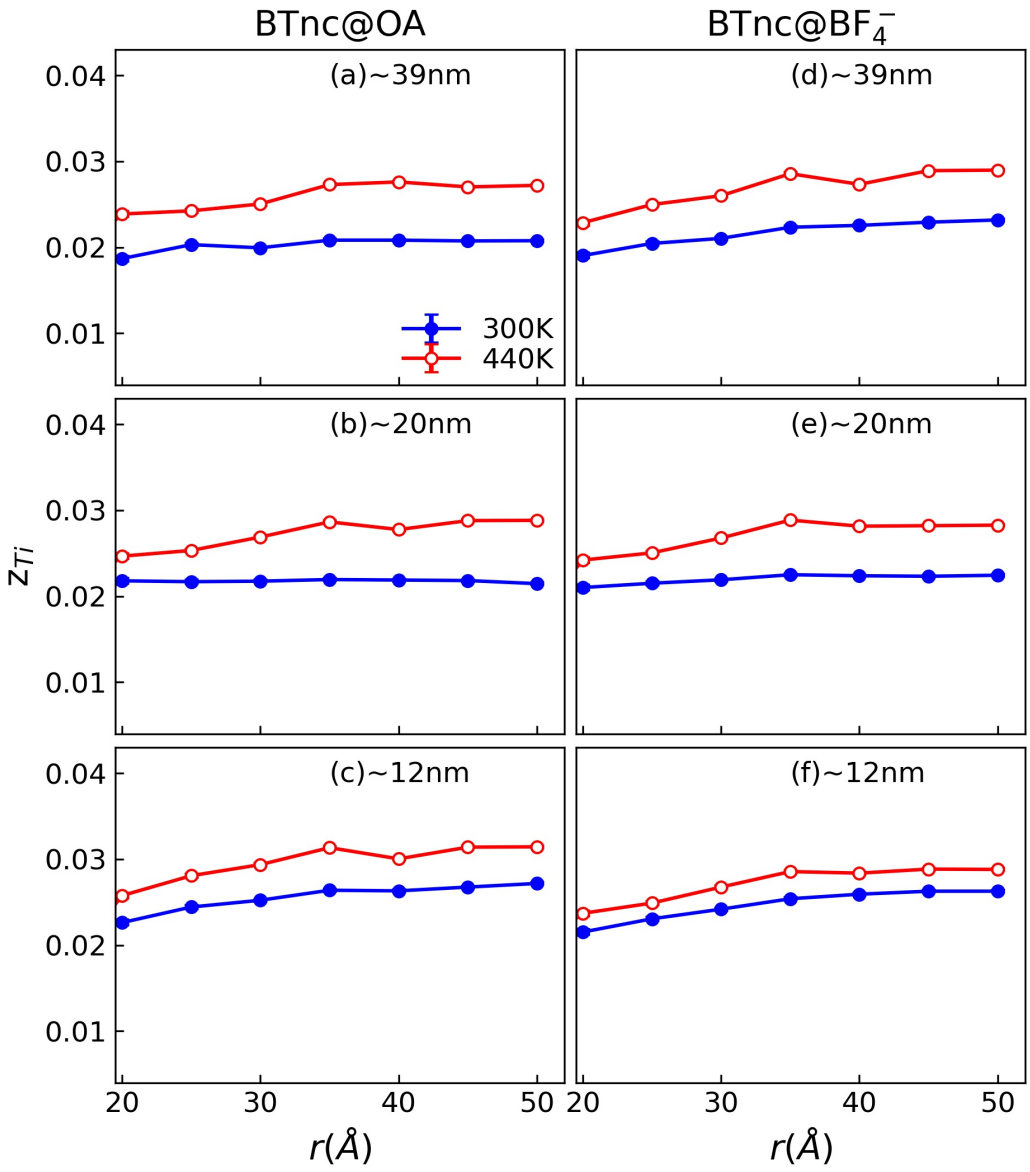

Figure S7: Ti off-centering (z_{Ti}) parameter resulting from PDF refinements using non-centrosymmmetric tetragonal $P4mm$ model with varying r_{max} range from 20 Åto 50 Å. Blue symbols indicate 300 K data and red symbols indicate 440 K data.

Table S1: Goodness of fit (R_w) of PDF refinements of synchrotron X-ray data over 1.5-10 Å and 10-50 Å ranges using centrosymmmetric cubic $Pm\bar{3}m$, and non-centrosymmmetric (tetragonal $P4mm$, orthorhombic $Amm2$ and rhombohedra $R3m$) space groups at 300 K and 440 K. The orthorhombic $Amm2$ model was employed with oxygen position fixed to make the number of refined parameters close to that of the $P4mm$ model. The lowest R_w values resulting among the four applied models are highlighted in bold text for each specific temperature and range.

		BTnc@OA				BTnc@BF_4^-			
	Space group	1.5 to 10Å		10 to 50Å		1.5 to 10Å		10 to 50Å	
		300K	440K	300K	440K	300K	440K	300K	440K
∼39nm	$Pm\bar{3}m$	26.73	25.65	19.70	18.61	20.15	18.34	12.96	12.77
	$P4mm$	**26.24**	**25.19**	**17.76**	18.02	**19.74**	17.87	**11.54**	11.89
	$Amm2$	27.96	25.77	18.07	**17.99**	20.99	18.03	11.67	**11.87**
	$R3m$	26.36	25.24	19.84	21.79	19.78	**17.86**	13.69	17.46
∼20nm	$Pm\bar{3}m$	20.56	18.49	14.23	12.14	19.95	17.61	12.63	12.35
	$P4mm$	**20.03**	18.07	**11.37**	**11.68**	**19.40**	17.35	**10.95**	11.48
	$Amm2$	20.54	18.08	11.77	**11.68**	19.85	17.21	11.13	**11.46**
	$R3m$	20.19	**18.03**	14.64	17.22	19.55	**17.19**	13.33	17.18
∼12nm	$Pm\bar{3}m$	19.15	17.35	12.84	12.75	17.48	16.76	11.58	11.05
	$P4mm$	**18.58**	16.95	11.86	11.79	**16.94**	16.50	10.29	10.09
	$Amm2$	**18.58**	**16.89**	**11.85**	**11.78**	16.98	**16.41**	**10.28**	**10.06**
	$R3m$	18.92	17.23	14.99	17.23	17.25	16.59	14.21	18.66

Table S2: Atomic displacement parameters (ADP, U_{iso} (Å)) for Ti atoms of PDF refinements of synchrotron X-ray data over 1.5-10 Å and 10-50 Å ranges using centrosymmmetric cubic $Pm\bar{3}m$, and non-centrosymmmetric (tetragonal $P4mm$, orthorhombic $Amm2$ and rhombohedra $R3m$) space groups at 300 K and 440 K. The lowest ADP values resulting among the four applied models are highlighted in bold text for each specific temperature and range.

		BTnc@OA				BTnc@BF_4^-			
	SG	1.5 to 10Å		10 to 50Å		1.5 to 10Å		10 to 50Å	
		300K	440K	300K	440K	300K	440K	300K	440K
∼39nm	$Pm\bar{3}m$	0.0080(4)	0.0096(4)	0.0082(1)	0.0089(1)	0.0087(3)	0.0105(3)	0.0084(1)	0.0093(1)
	$P4mm$	**0.0056(11)**	**0.0066(14)**	0.0053(2)	0.0045(5)	**0.0062(8)**	**0.0076(10)**	0.0052(1)	0.0047(4)
	$Amm2$	0.0099(8)	0.0088(17)	**0.0045(2)**	**0.0044(5)**	0.0100(7)	0.0084(9)	**0.0045(2)**	**0.0046(4)**
	$R3m$	0.0078(4)	0.0082(11)	0.0079(2)	0.0078(1)	0.0080(6)	0.0084(7)	0.0078(1)	0.0078(1)
∼20nm	$Pm\bar{3}m$	0.0086(3)	0.0103(3)	0.0090(1)	0.0094(1)	0.0085(3)	0.0102(3)	0.0084(1)	0.0093(1)
	$P4mm$	**0.0059(9)**	**0.0067(10)**	0.0060(1)	0.0048(4)	**0.0059(8)**	**0.0066(9)**	0.0053(1)	0.0046(4)
	$Amm2$	0.0089(5)	0.0073(11)	**0.0048(2)**	**0.0047(4)**	0.0069(9)	0.0074(12)	**0.0043(2)**	**0.0046(4)**
	$R3m$	0.0078(6)	0.0092(6)	0.0081(1)	0.0081(1)	0.0082(7)	0.0082(8)	0.0079(1)	0.0080(1)
∼12nm	$Pm\bar{3}m$	0.0097(3)	0.0113(3)	0.0105(1)	0.0116(1)	0.0097(3)	0.0111(3)	0.0100(1)	0.0113(1)
	$P4mm$	0.0066(7)	0.0080(10)	0.0054(3)	0.0055(4)	**0.0072(6)**	**0.0089(8)**	0.0049(2)	0.0053(3)
	$Amm2$	**0.0066(9)**	**0.0067(11)**	**0.0052(3)**	**0.0054(4)**	0.0074(7)	0.0090(9)	**0.0047(2)**	**0.0052(3)**
	$R3m$	0.0100(6)	0.0099(8)	0.0076(1)	0.0077(1)	0.0090(5)	0.0110(4)	0.0077(1)	0.0075(1)