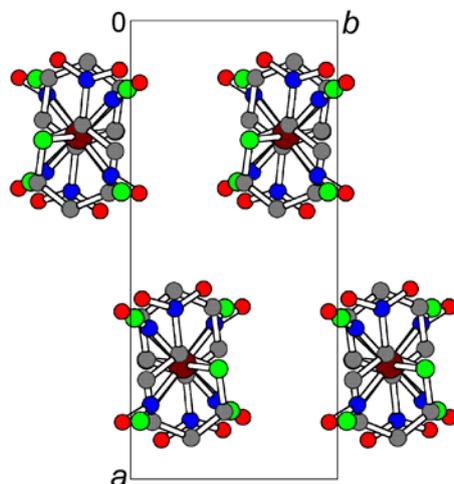


## Supplementary Information

**Figure S1.** Projection of the anion layer in the structure **1** along the  $c$ -axis.



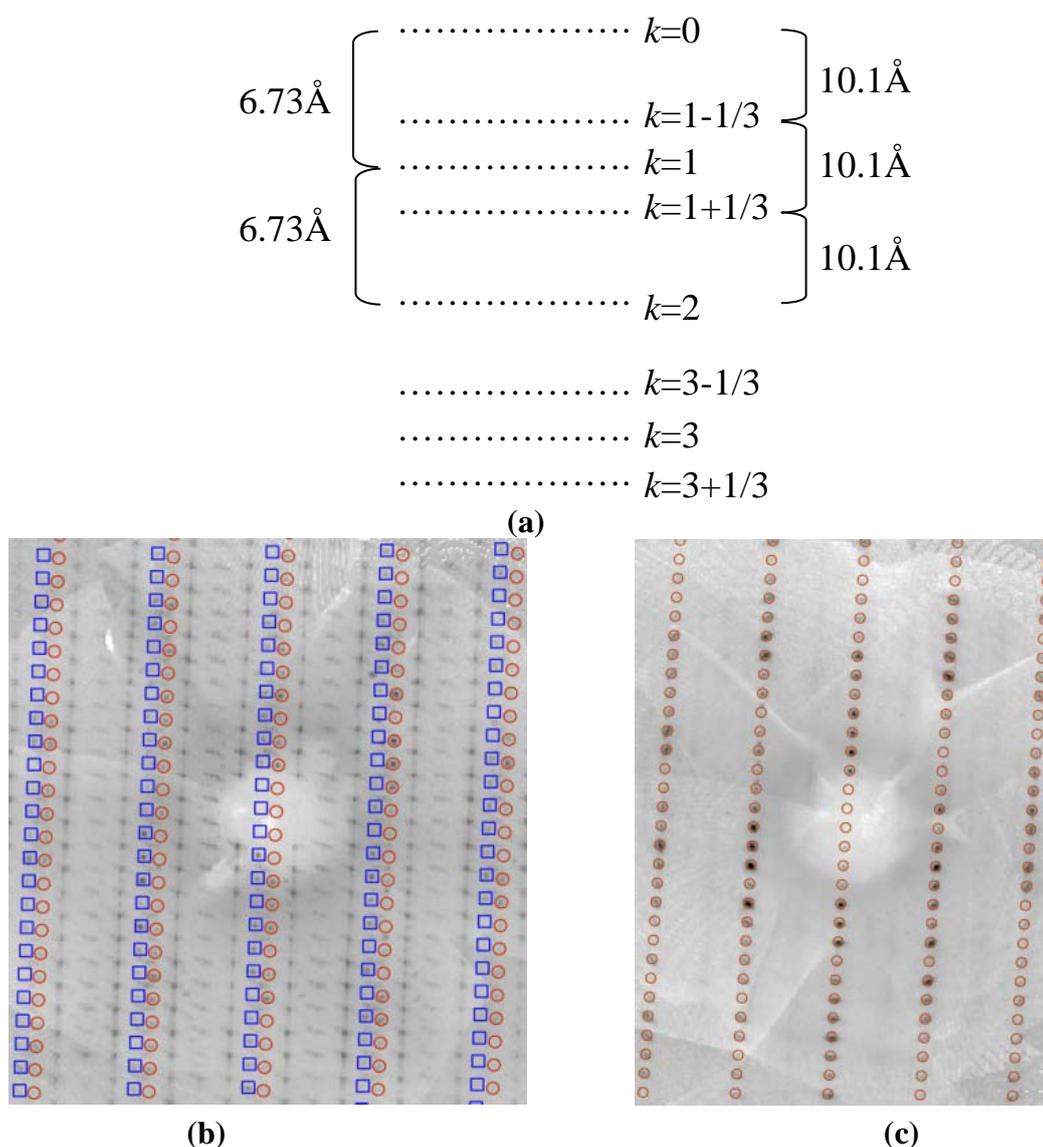
### X-ray Diffraction Study of the Superstructure in the $\delta$ -(BEDT-TTF)<sub>4</sub>[OsNOCl<sub>5</sub>]<sub>1.33</sub>(C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>)<sub>0.67</sub> (1) Crystal

$\delta$ -(BEDT-TTF)<sub>4</sub>[OsNOCl<sub>5</sub>]<sub>1.33</sub>(C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>)<sub>0.67</sub> crystals from two similar syntheses (batches 1 and 2) were investigated by X-ray diffraction. Superstructure was found on Weissenberg photographs of the crystals from batch 1 while in the crystals from batch 2 such superstructure was not observed. Additional lines of weak and diffuse diffraction peaks correspond to triplication of the shortest lattice translation  $b$ ,  $6.73 \text{ \AA} \times 3 = 20.2 \text{ \AA}$ . However, this is not a simple triplication, because the superstructural planes are observed only near the main planes of the reciprocal lattice with odd  $k$ -indices, i.e. additional  $hkl$  peaks have  $k = 2n + 1 \pm 1/3$ . The schematic representation of the X-ray film obtained by rotation of the crystal around the monoclinic  $b$ -axis is shown in Figure S2a, and the reconstructed  $(h2/3l)$  experimental reciprocal planes for the crystals with and without superstructure are shown in Figures S2b and S2c, respectively. The pattern in Figure S2a can be described by two separate lattices with different translation parameters. One lattice with  $b = 6.73 \text{ \AA}$  well reproduces the strict periodicity of the donor sublattice while additional reflections with  $b = 10.1 \text{ \AA}$  can be associated with the real periodicity of the anion layer which is disordered in the lattice with  $b = 6.73 \text{ \AA}$ . Thus, the periodicity of the donor sublattice  $b_{\text{donor}}$  is not a multiplied periodicity of the anion layer  $b_{\text{anion}}$  but  $3b_{\text{donor}} = 2b_{\text{anion}}$  and two systems of diffraction peaks meet on the reciprocal planes with even  $k$ -indices (0, 2, 4, ...).

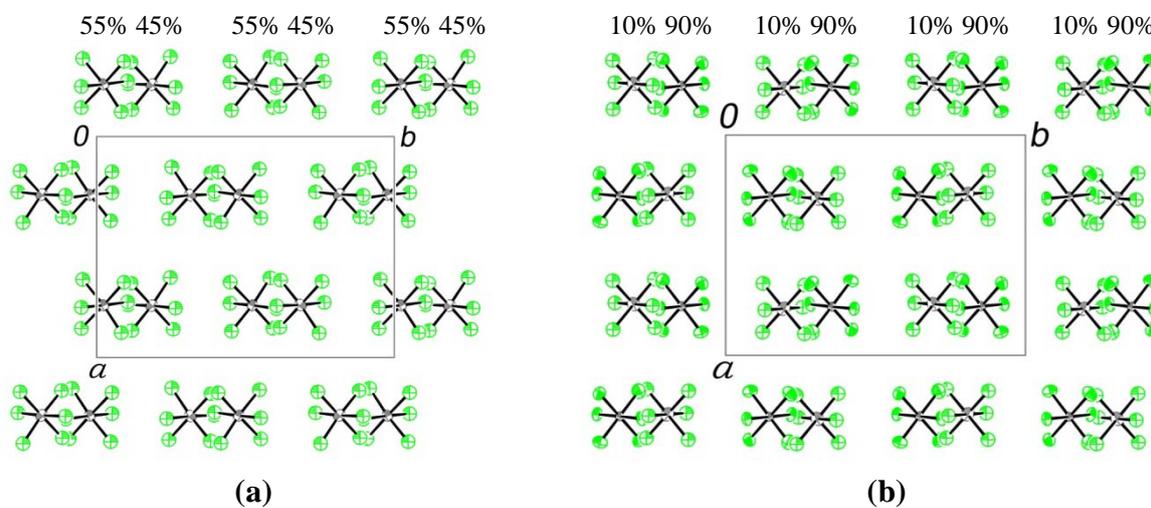
The average structure (for  $b = 6.73 \text{ \AA}$ ) of the crystals from batch 1 possesses itself different symmetry ( $P2_1/a$ ) in comparison with crystals without superstructure from the batch 2 ( $I2/a$ ). Systematic absences corresponding to  $I$ -centering disappear and periodicity of the disordered infinite anion chain along the channel in the  $P$ -lattice becomes  $3.35 \text{ \AA}$ , i.e.  $b/2$ . An attempt to include into refinement superstructural peaks did not lead to the ordered structure although one could expect a complete ordering of two anions and one solvent molecule on the triple period of  $20.2 \text{ \AA}$ . Instead we obtained two different anion layers (Figures S3a and S3b). They are composed by similar chains of close anion pairs with different degree of adjacent sites occupation. The effective lattice parameter along the monoclinic axis in the triple lattice is indeed  $10.1 \text{ \AA}$  instead of  $6.7 \text{ \AA}$  in both the layers;

however, the mutual arrangement of the adjacent chains differs in two layers. Although the structure refinement in triple lattice gave only rough results, because the X-ray data processing was complicated by the presence of the twinned  $\beta''$ -salt as well as the  $\delta$  phase with the superstructure, two general conclusions can be made. First, molecules inside the mixed anion-solvent chains are very mobile and, second, adjacent chains are weakly sensitive to each other and can move independently. It should be emphasized that the rough structural model allows explaining the appearance of the superstructure by displacement of the anions from their average positions (shown in Figure S1) along the direction of triple translation.

**Figure S2.** (a) Schematic representation of the X-ray image from the  $\delta$ -type crystal from batch 1 rotating around the monoclinic axis. Two independent lattice periods of 6.73 and 10.1 Å can be associated with the periodicity of the donor and anion layers, respectively. Reconstructed reciprocal layers ( $h2/3l$ ) in  $\delta$ -crystals with superstructure from batch 1 (b) and without it from batch 2 (c). Red circles and blue squares mark reflections from  $\beta''$ -lattices twinned in crystals with superstructure.



**Figure S3.** Projections of two independent anion layers in the structure **1** (batch 1) refined in the triple lattice taking into account the superstructural diffraction reflections. Occupations of the disordered anion positions are shown in percentage terms.



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