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MATERIALS

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**Supporting information for article:**

**Phase transition sequences in tetramethylammonium tetrachloro-  
metallates by X-ray diffraction and spectroscopic measurements**

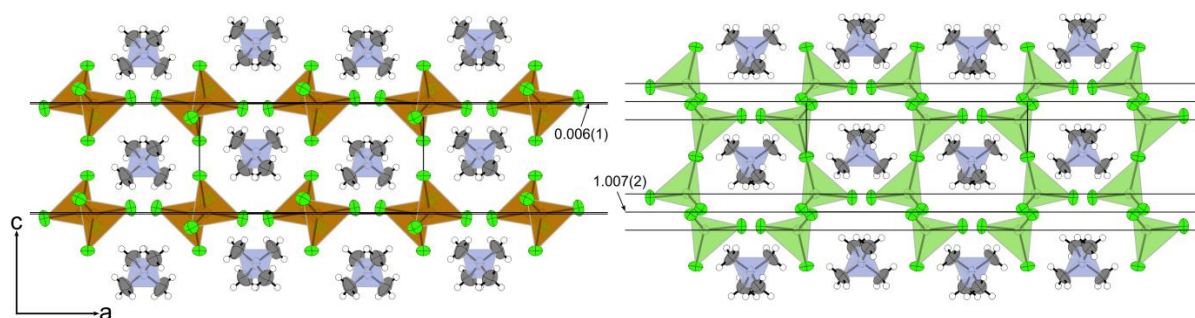
**Jack Binns, Garry J McIntyre, José A. Barreda-Argüeso, Jesús González,  
Fernando Aguado, Fernando Rodríguez, Rafael Valiente and Simon Parsons**

**S1. Twin indexing****Table S1** Indexing information for twinned phases of TCF and TCG

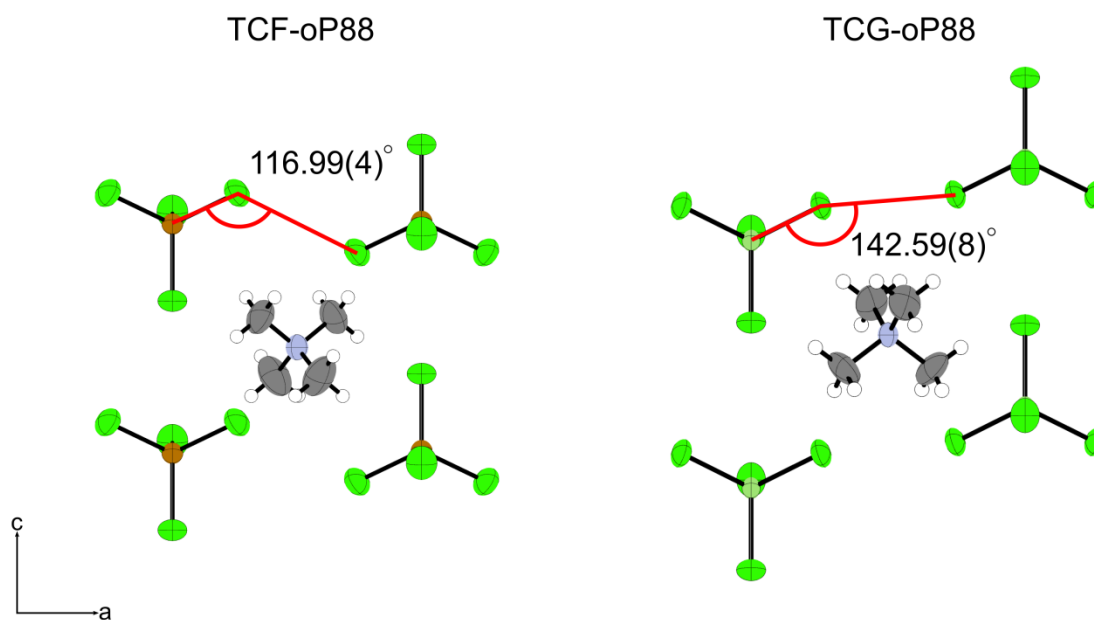
Phase	Temperature	No. reflections indexed to domain 1	No. reflections indexed to domain 2	No. overlapping reflections
TCF- <i>mP22</i>	318	1046	899	1635
TCF- <i>mP44</i>	365	2012	1941	1907
TCG- <i>oP88</i>	226	6412	822	3370
TCG- <i>mP22</i>	300	2204	723	1656

**S2. Crystal packing and thermal expansion**

(a)



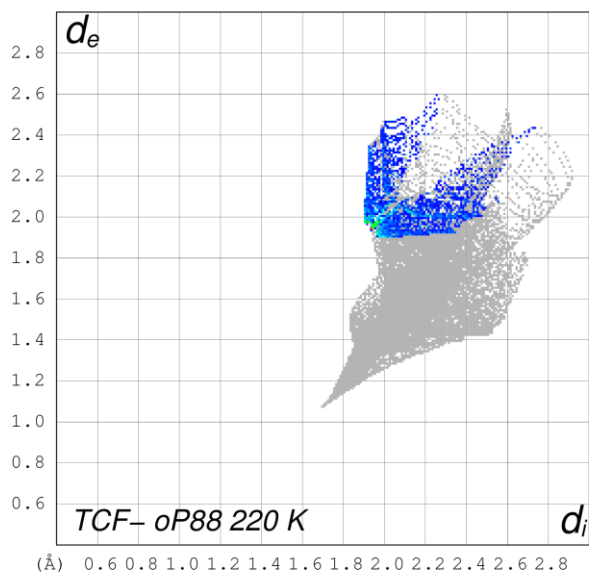
(b)



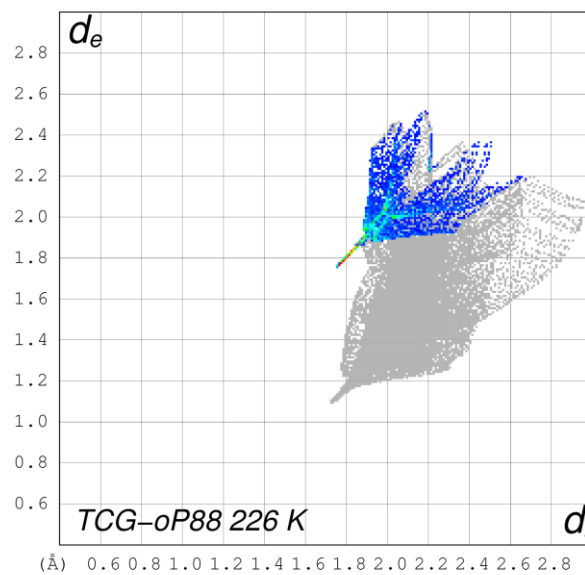
**Figure S1** (a) Crystal structure projections of TCF-*oP88* (left) and TCG-*oP88* (right) illustrating the significant off-sets in [GaCl<sub>4</sub>]<sup>-</sup> anionic positions; (b) *M*-Cl...Cl short-contact angles in *oP88* phases, as a result of more covalent-type interaction the Ga-Cl...Cl contact is significantly more linear.

**S3. Fingerprint plots**

(a)



(b)



**Figure S2** Fingerprint plots for (left)  $[\text{FeCl}_4]^-$  at 220 K and (right)  $[\text{GaCl}_4]^-$  at 226 K. Only Cl...Cl close contacts are highlighted. The sharp 'point' at low  $d$  for TCG shows the prevalence of short Cl...Cl contacts in the structure.