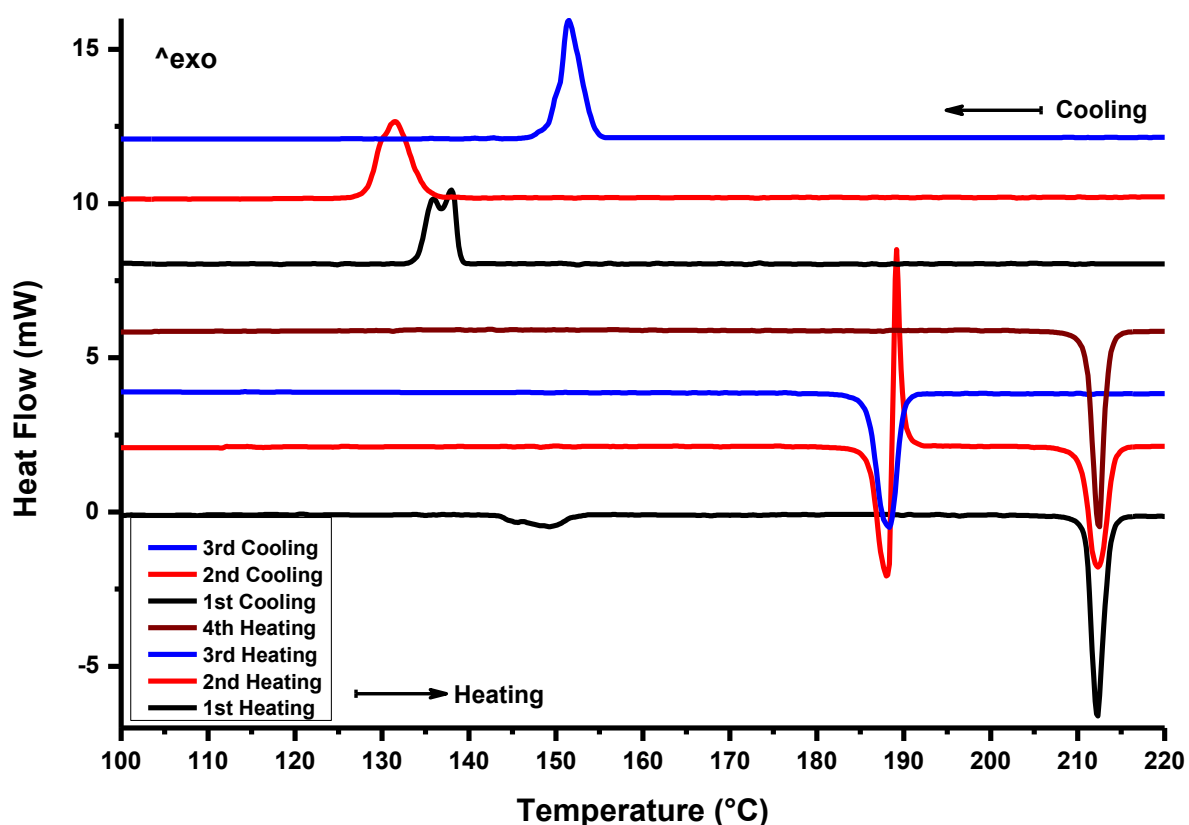


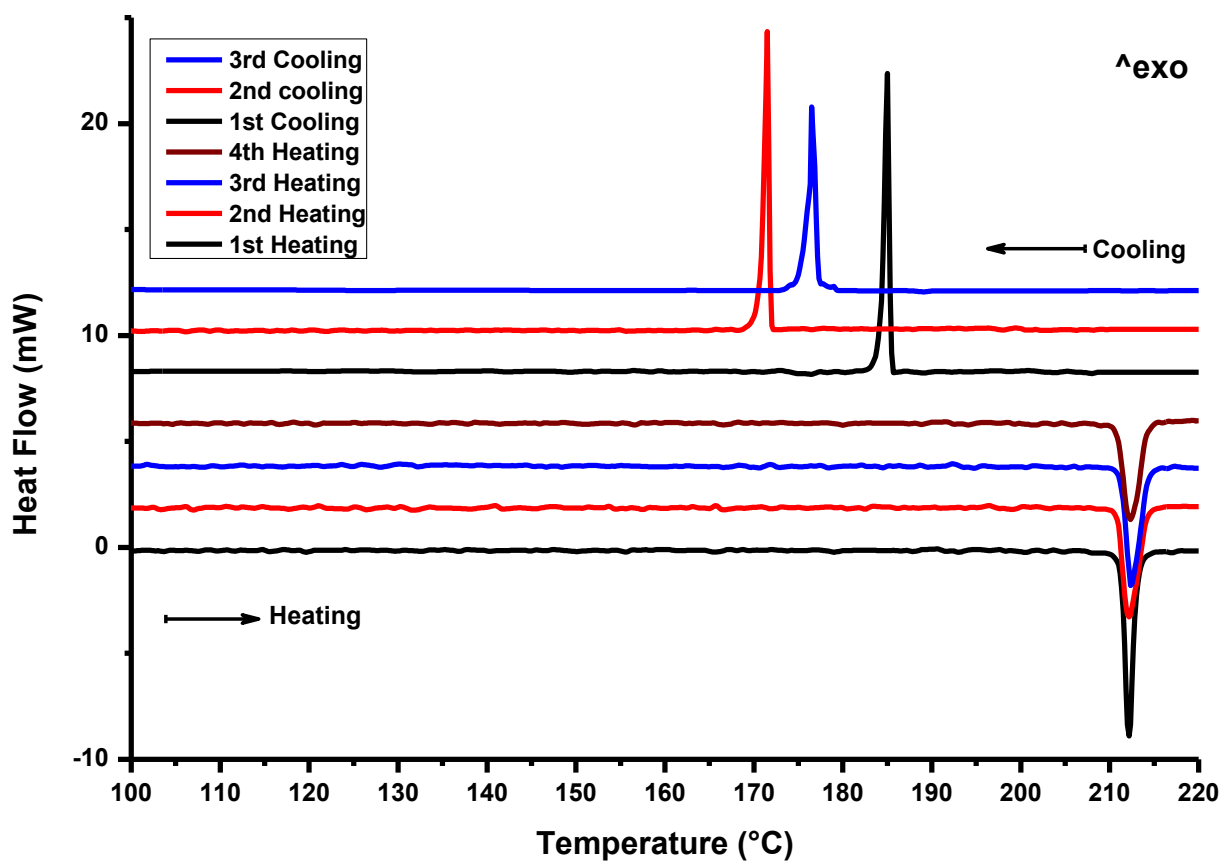
## Supplementary Material

### Enantiotropic Conformational Polymorphism in 2,2,4,4-bis-(2',2'-dimethylpropane-1',3'-dioxy)-6,6-dichlorocyclotriphosphazene

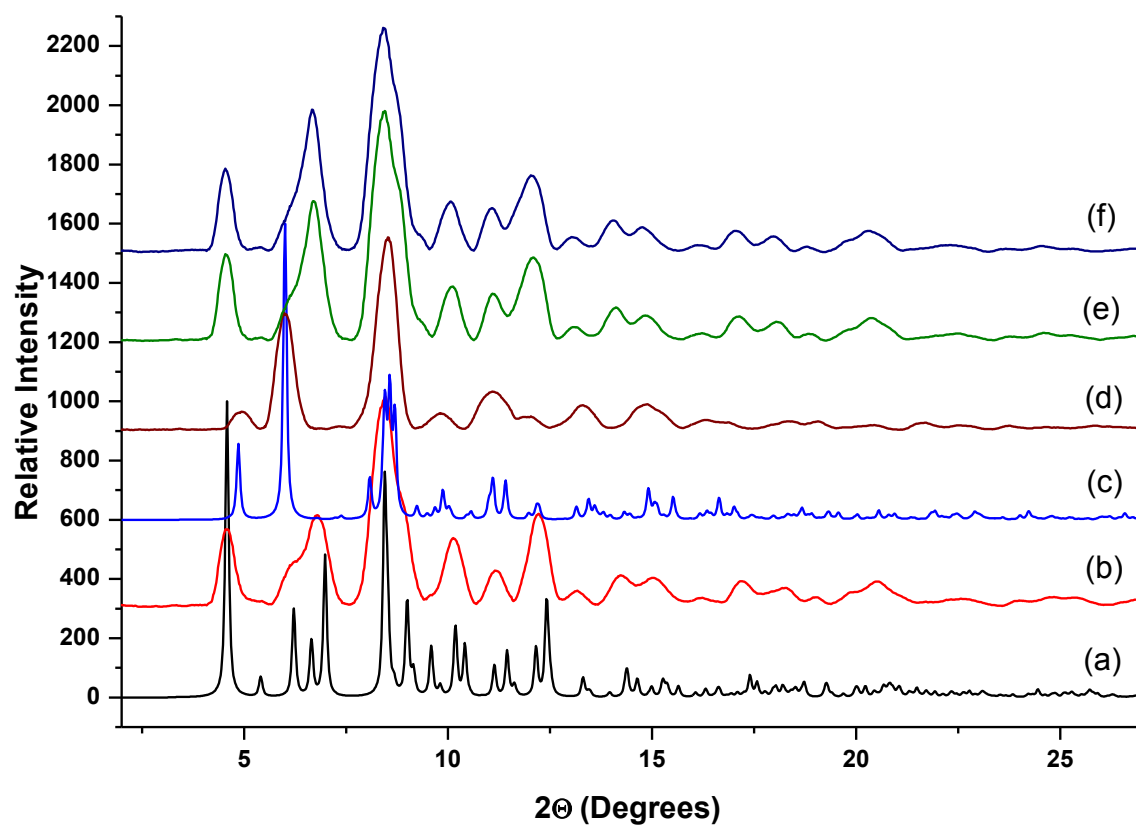
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**Figure 1s.** Annealed ( 3 heating followed by 3 cooling and 4<sup>th</sup> heating) DSC measurement of  $\beta$  form. Data were observed between 25-220°C but here only the 100-220°C region is displayed for clarity.



**Figure 2s.** Annealed ( 3 heating followed by 3 cooling and 4<sup>th</sup> heating) DSC measurement of  $\alpha$  form. Data were observed between 25-220°C but here only the 100-220°C region is displayed for clarity.



**Figure 3s.** Overlaid XRPD patterns; **a)** simulated powder pattern of  $\beta$  form, **b)** XRPD of powdered fresh  $\beta$  form sample at 25°C, **c)** simulated powder pattern of  $\alpha$  form, **d)** XRPD of sample at 150°C after phase transition, **e)** XRPD of the sample at 120° (after melting at 212°C and crystallized at 140°C), **f)** XRPD of the sample at 186°C (just before melting).