

Figure S1. The custom built micro-vacuum box

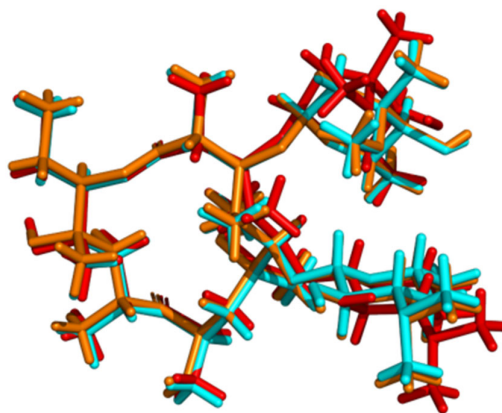


Figure S2. The conformation overlays diagram of CLA Form 0' (cyan), Form II (red) and CLA-Eth solvate (orange).

Table S1. Crystallographic data of CLA-Eth solvate

Phase	CLA-Eth solvate
empirical formula	$C_{38}H_{69}NO_{13} \cdot C_6H_{12}O_2$
formula weight	840.08
crystal system	orthorhombic

space group	P 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
temperature (°C)	0
<i>a</i> (Å)	8.7685(9)
<i>b</i> (Å)	14.5980(16)
<i>c</i> (Å)	38.368(4)
$\alpha$ (°)	90
$\beta$ (°)	90
$\gamma$ (°)	90
cell volume (Å <sup>3</sup> )	4911.2(9)
<i>Z</i>	4
$\rho$ , kg·m <sup>-3</sup>	1.136
R <sub>int</sub>	0.0799
R1 ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0573
wR <sub>2</sub>	0.1501
CCDC NO	700729

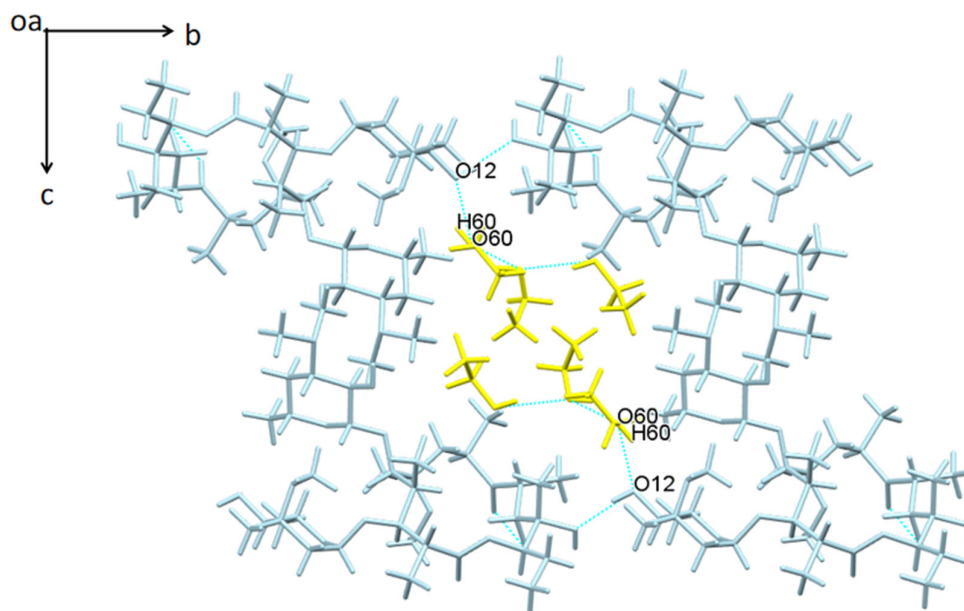


Figure S3. Molecular arrangement of CLA-Eth solvate crystal structure

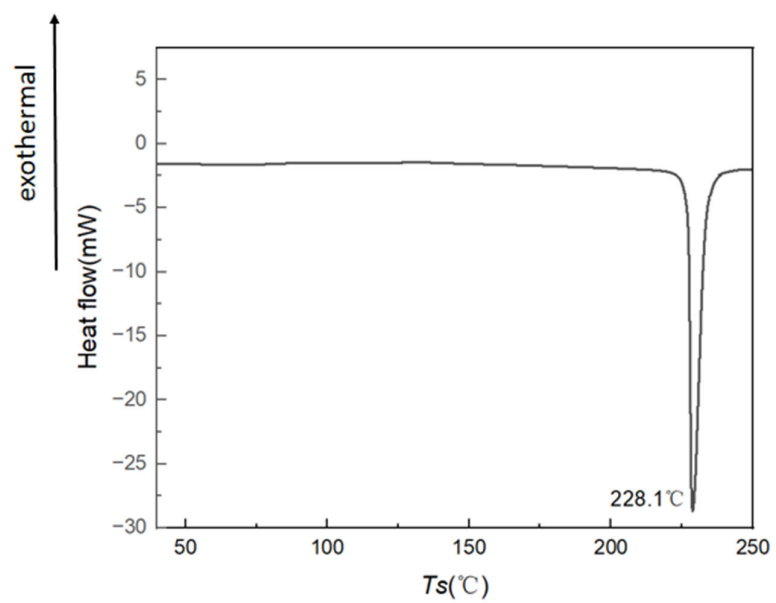


Figure S4. DSC curve of CLA raw material

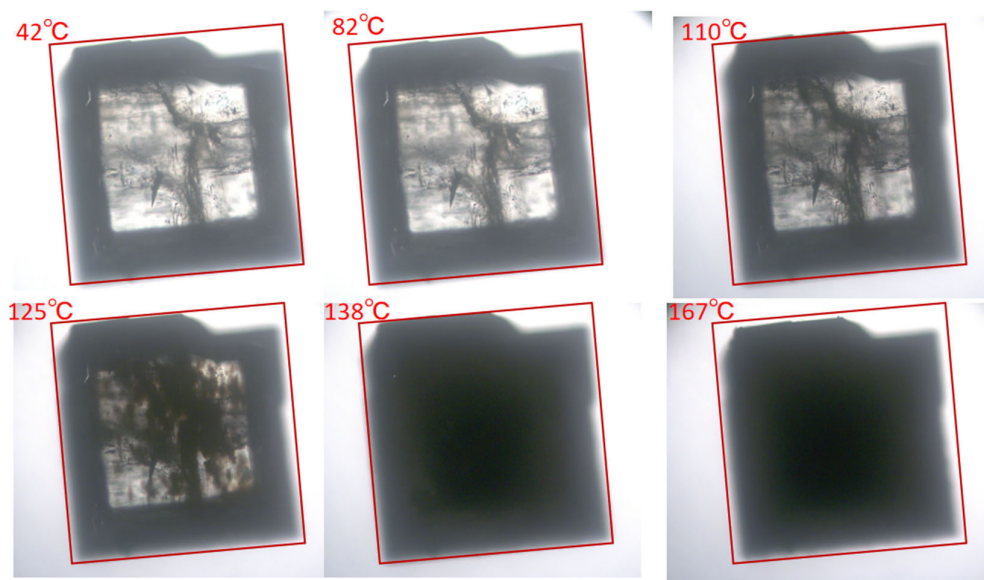


Figure S5. HSM snapshots of CLA-PAC solvate.

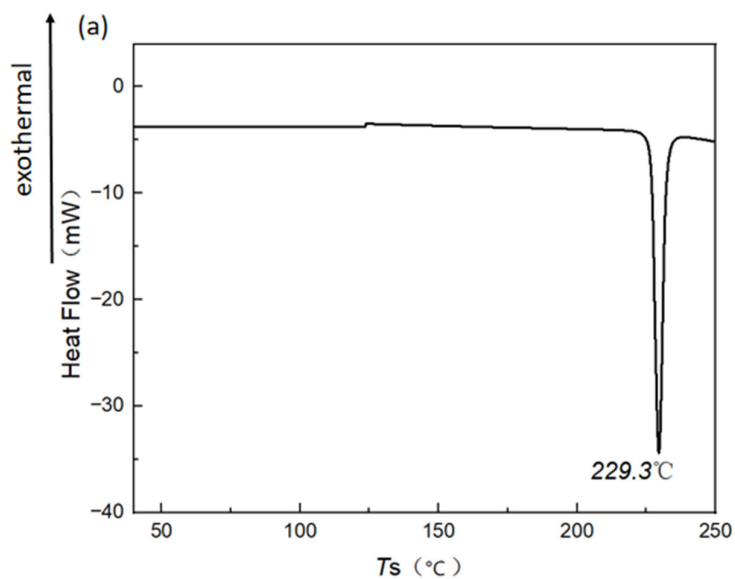


Figure S6. DSC curve of the sample after the observation experiment by HSM

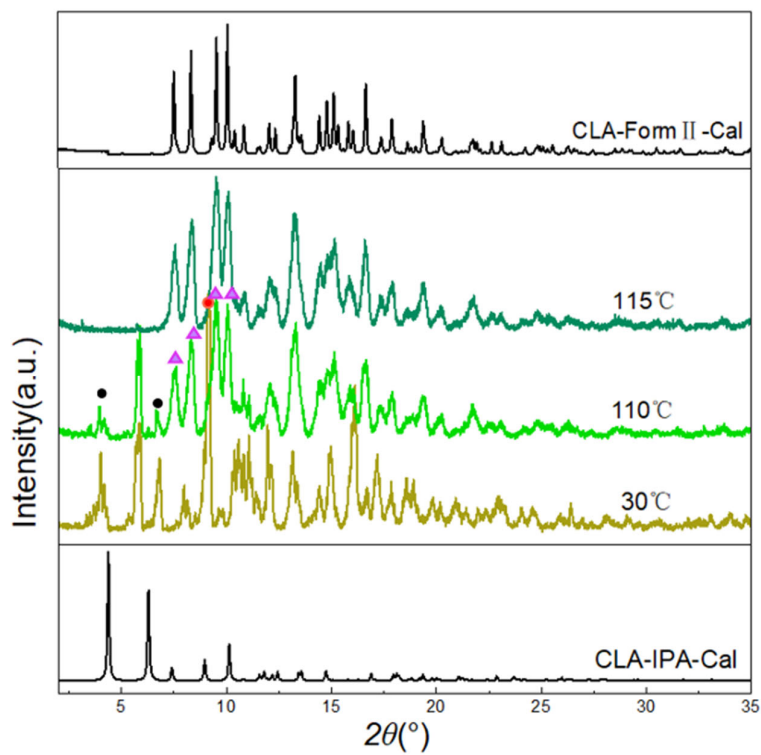


Figure S7. VT-PXRD of CLA-IPA solvate

The VT-PXRD of CLA-IPA solvate is shown in Figure S7. It can be found that when heating to 110 °C, four peaks of Form II at the position of  $2\theta = 8.445^{\circ}$ ,  $9.363^{\circ}$ ,

10.748°, 11.356° (marked as purple triangle) appear. At the same time, the diffraction peak of the CLA-IPA solvate at  $2\theta = 10.106^\circ$  (marked as red circle) disappears, and the intensities of the diffraction peak at  $2\theta = 4.601^\circ$  and  $7.607^\circ$  (marked as black circle) decrease. When the temperature continues to rise to 115°C, the characteristic peak of the CLA-IPA solvate at  $2\theta = 6.492^\circ$  also disappears. Therefore, the first endothermic process of 109.67 °C ~ 130.83 °C on the DSC curve (Figure 3d) of CLA-IPA solvate corresponds to the desolvation and transformation of the solvate into Form II, and the second endothermic peak corresponds to the melting process of Form II.

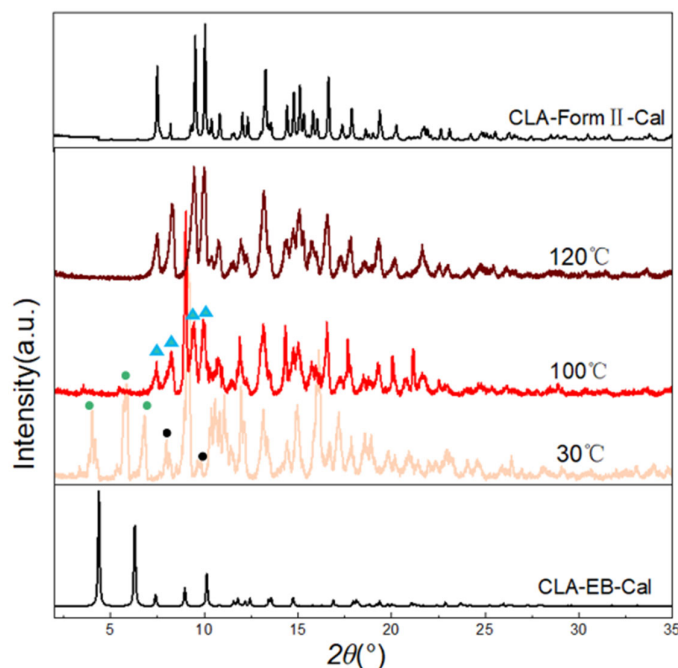
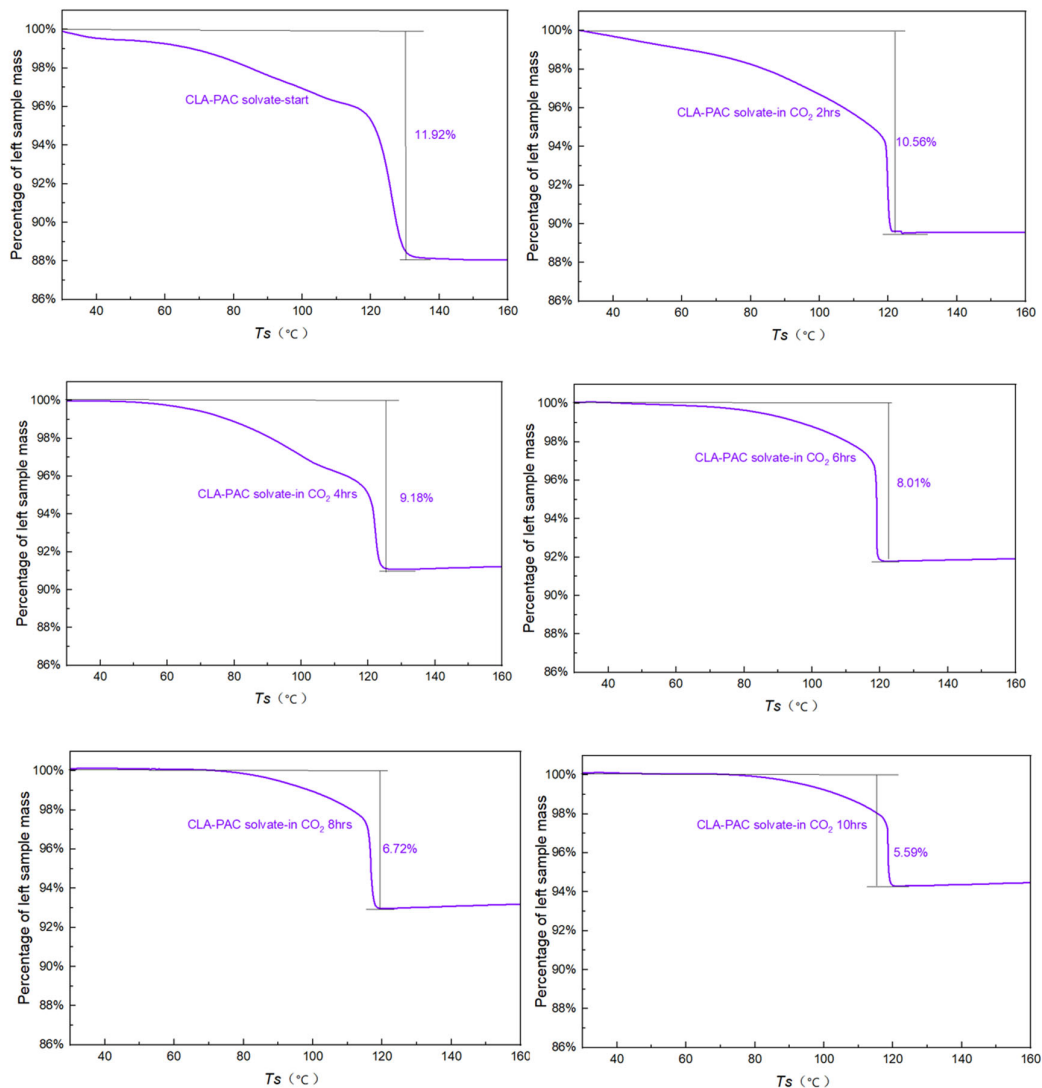


Figure S8. VT-PXRD of CLA-EB solvate

The VT-PXRD of CLA-EB solvate is shown in Figure S8. It can be observed that when the temperature rises to 100 °C, the diffraction peak of the CLA-EB solvate at  $9.194^\circ$  (marked as the black circle) develops into two diffraction peaks of Form II at  $8.445^\circ$  and  $9.363^\circ$ , and the diffraction peak at  $10.883^\circ$  (black circle mark) also evolves into two diffraction peaks of Form II at  $11.356^\circ$  and  $11.762^\circ$  (marked as the blue triangle mark). At the same time, the characteristic peaks of the CLA-EB solvate at  $2\theta = 4.601^\circ$ ,  $6.492^\circ$ ,  $7.607^\circ$  (see green circle mark) disappear. When the temperature continues to

rise to 120 °C, the characteristic peak of the CLA-EB solvate at  $2\theta = 10.106^\circ$  also disappears, indicating the solvate completely transforms into Form II. Therefore, on the DSC curve (Figure 3d) of CLA-EB solvate, the first endotherm at 99.33 °C ~ 133.83 °C solvate corresponds to the desolvation and transformation of the solvate into Form II, and the second endotherm corresponds to the melting process of Form II.



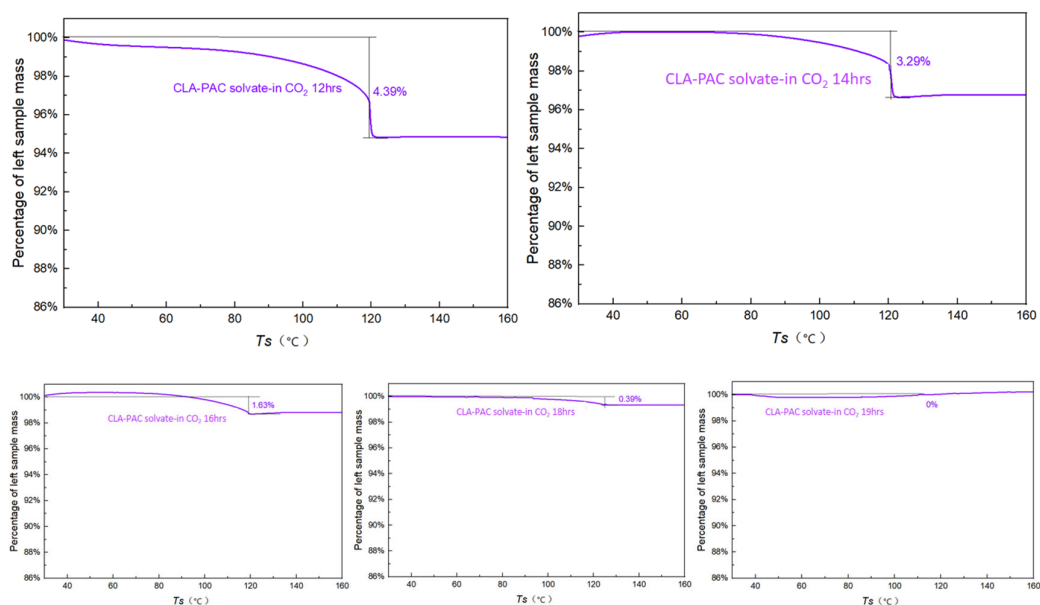
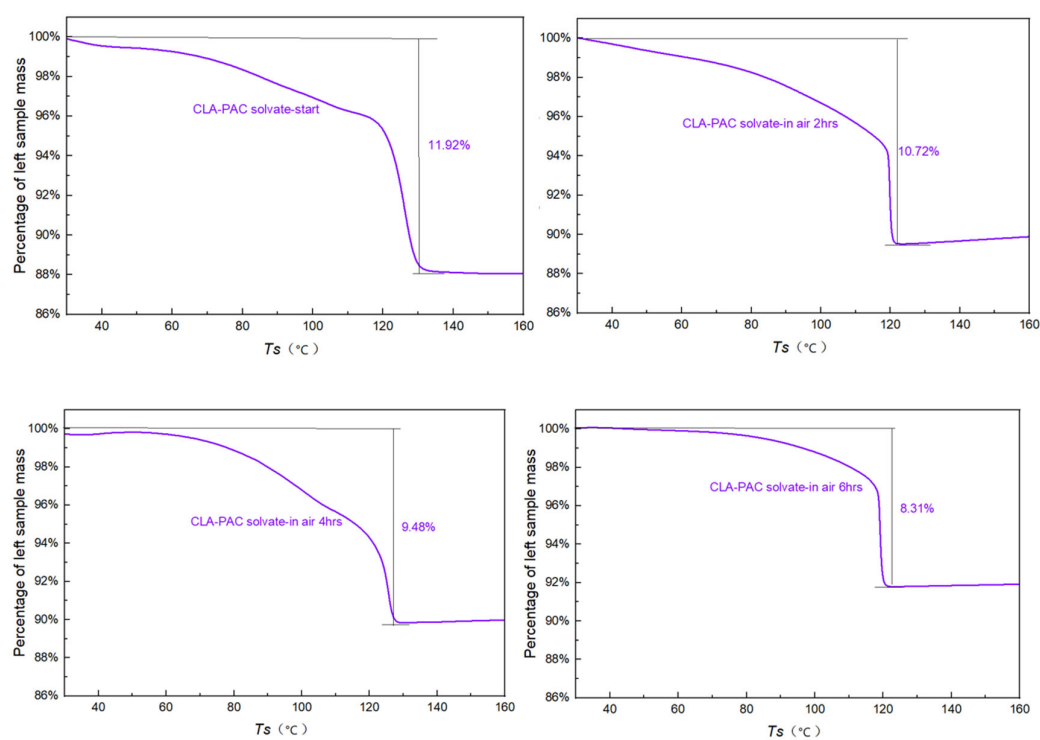


Figure S9. The solvent residual in the sample after heating at  $50^{\circ}\text{C}$  and 1atm  $\text{CO}_2$  for different duration



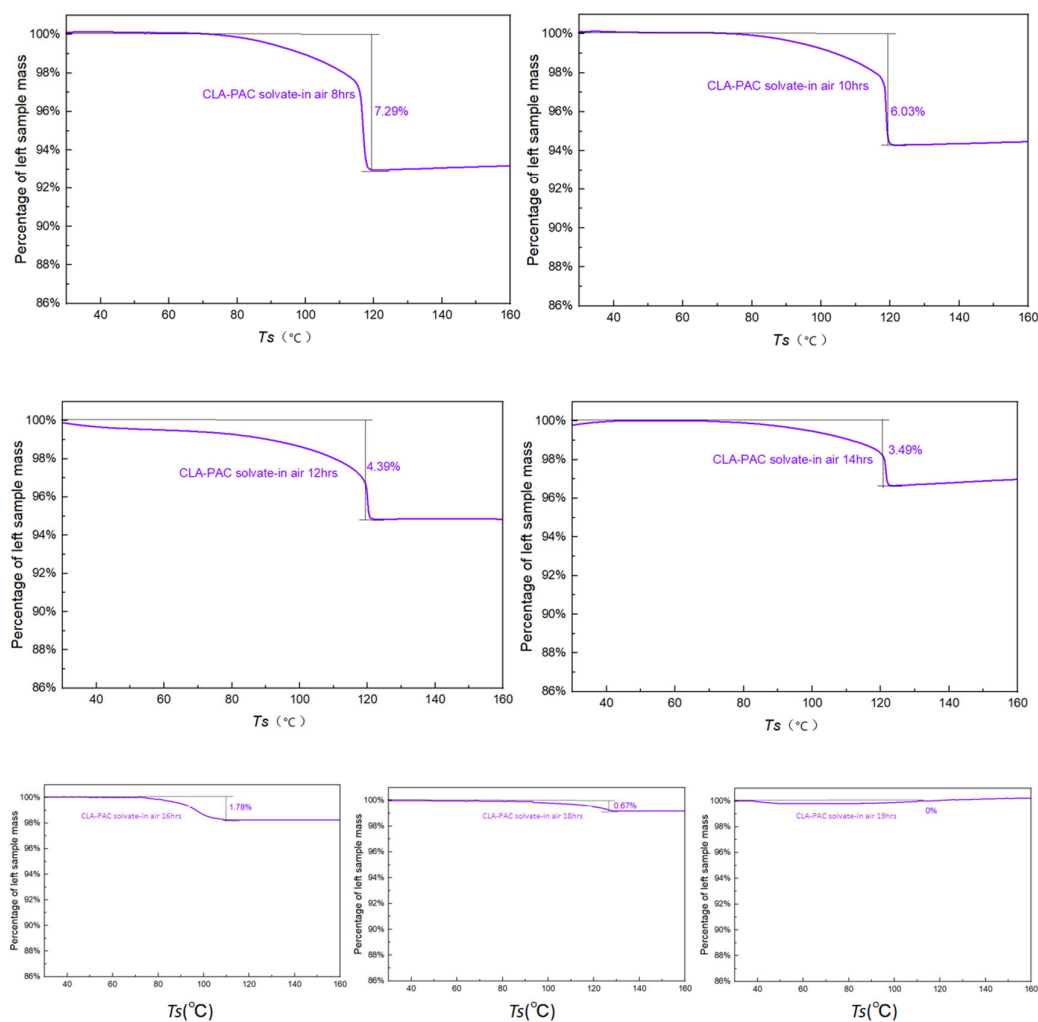


Figure S10. The solvent residual in the sample after heating at 50°C and 1atm air for different duration



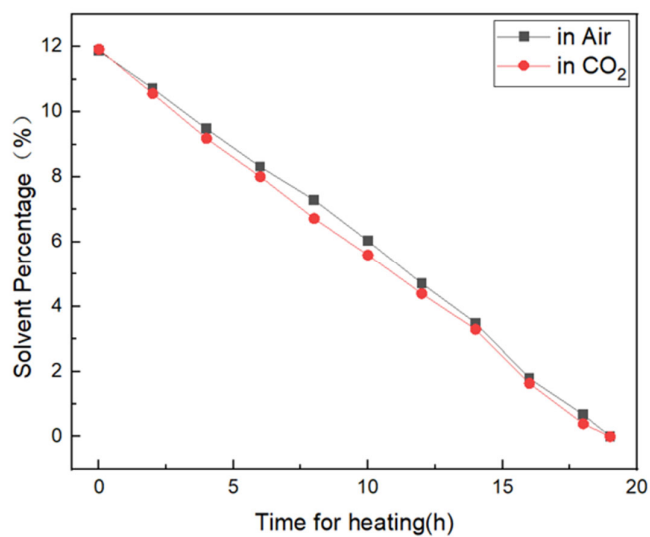


Figure S11. The change of solvent residual in CLA-PAC solvate with time

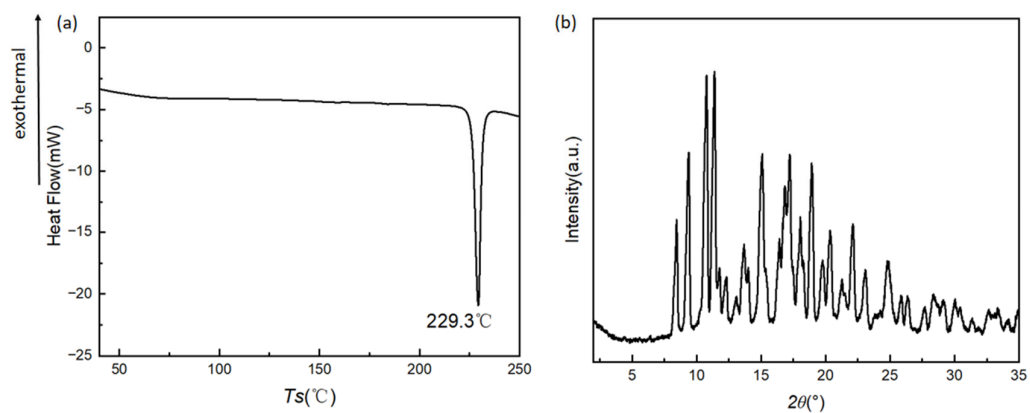


Figure S12. (a)DSC curve, (b)PXRD of the sample prepared by pathway.

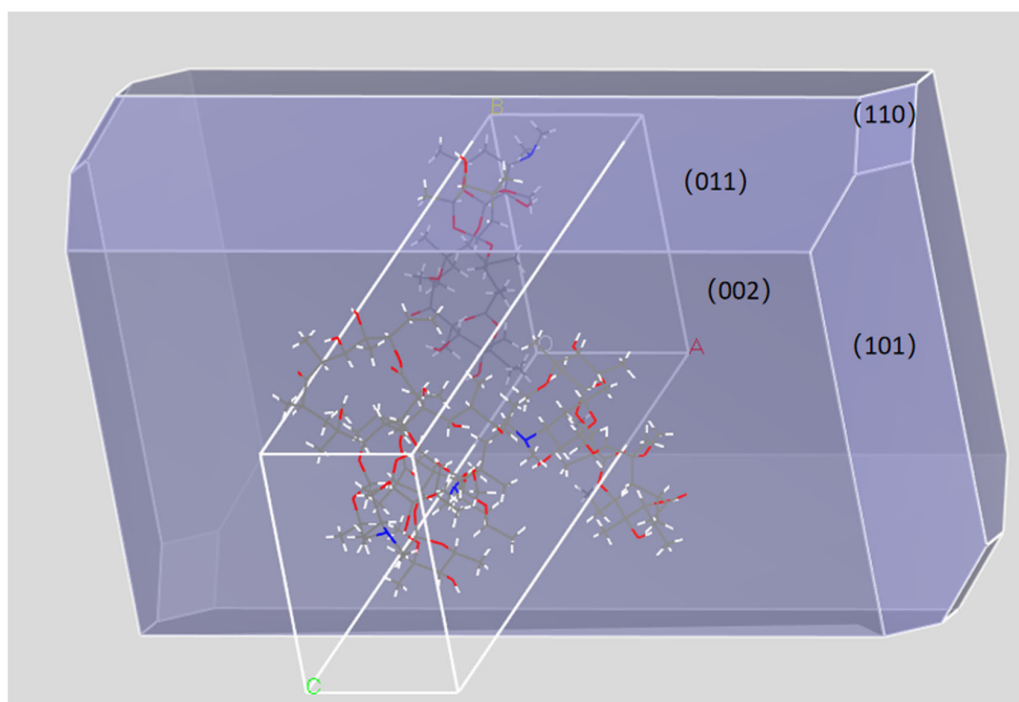


Figure S13. The morphology of CLA Form 0' predicted by BFDH model

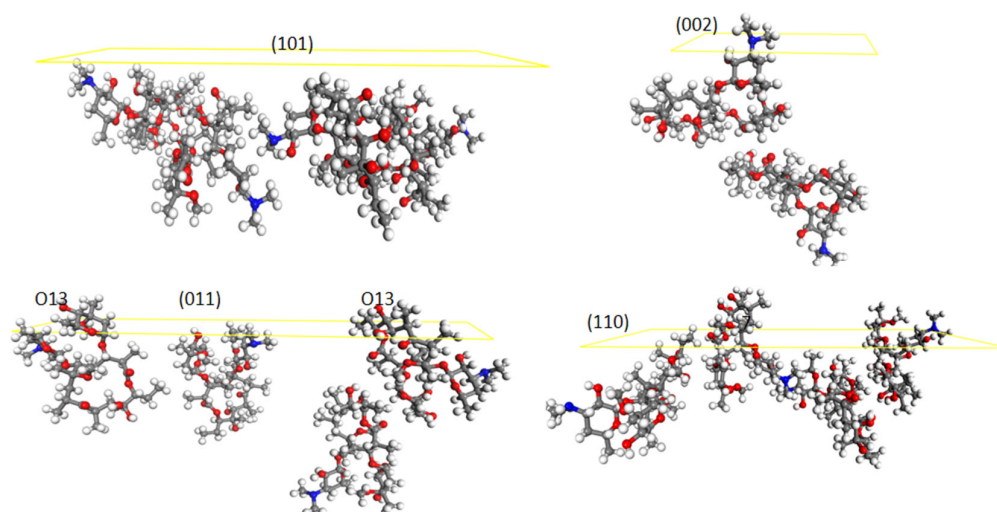


Figure S14. Molecular arrangements on crystal faces (101), (002), (011) and (110) of Form 0'

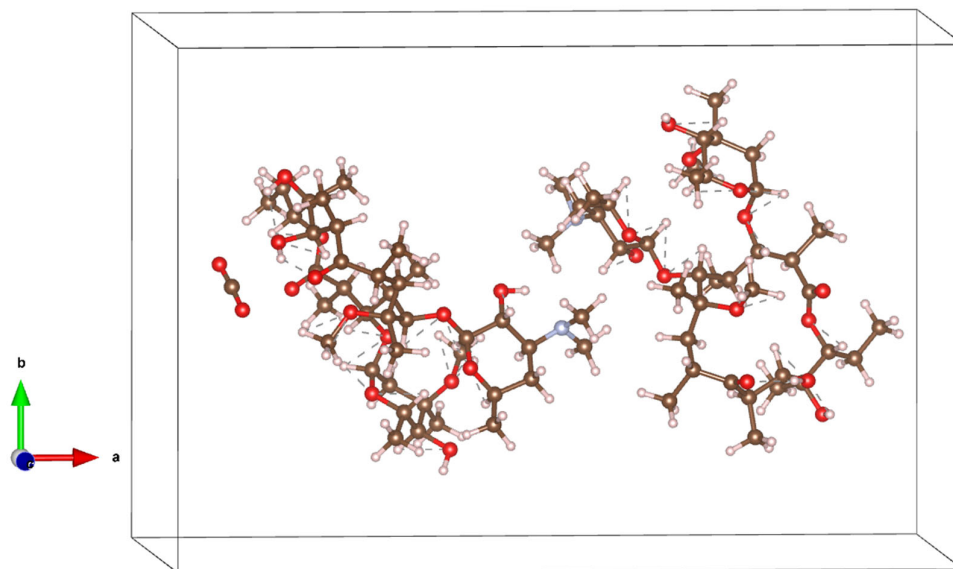


Figure S15. The model of the adsorption of CO<sub>2</sub> on Form 0' (Purple represents for N atoms, red for oxygen atoms, light pink for hydrogen atoms, and brown for carbon atoms)