Supporting Information

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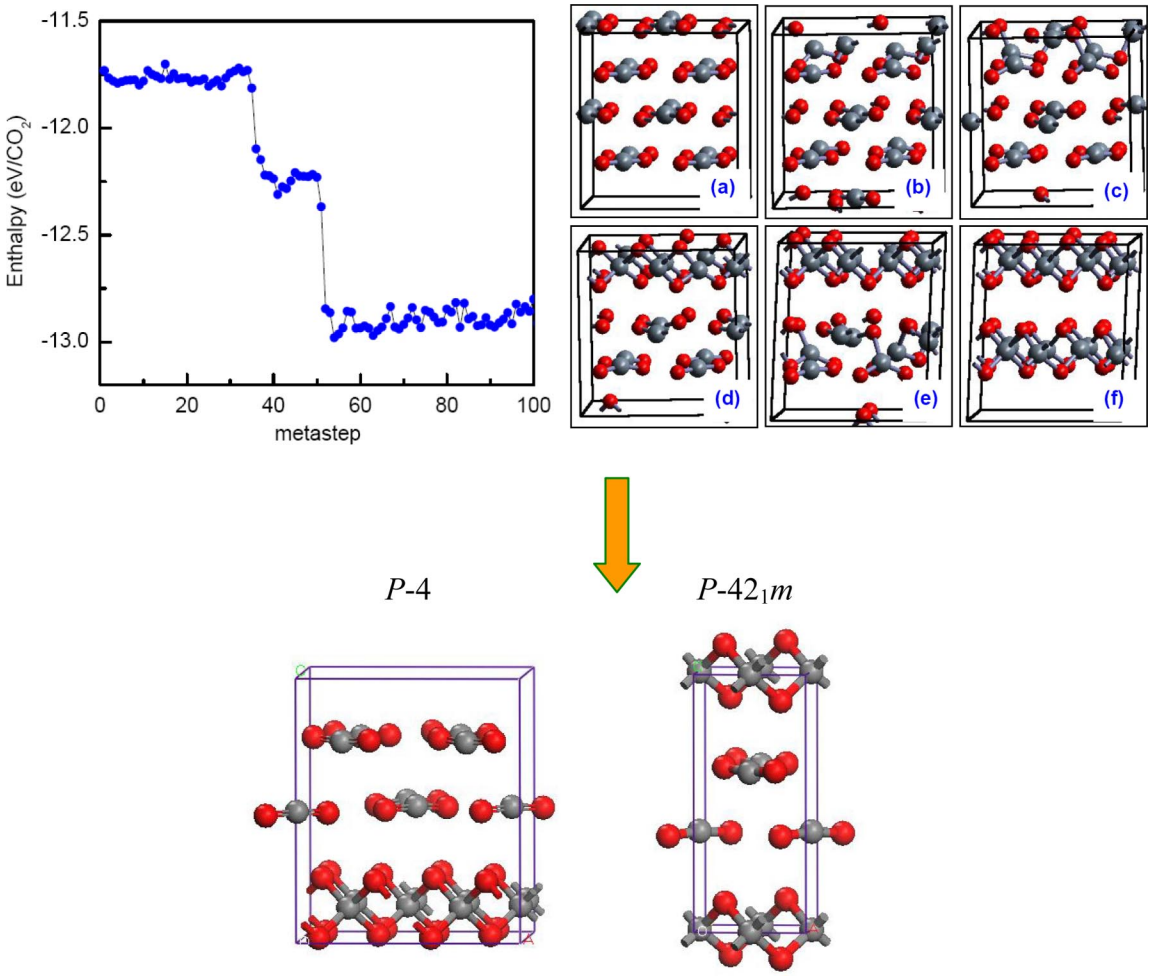

Fig. S1. Metadynamics simulation starting from Phase II ($P4_2/mnm$) at 60 GPa and 600 K with a 16 CO_2 molecules supercell. Gaussian parameters are width 20 (kbar·Å^3)$^{1/2}$ and height 400 kbar·Å^3. The enthalpy evolution shows an intermediate state at steps 41–49, the structure of this state is shown in *d*. After optimization, this half polymeric intermediate structure can be fit to *P*-4 or *P*-42$_1$m space group. The simple one (*P*-42$_1$m) is used to calculate the Raman spectra as a representative for the partially polymeric intermediate state between phase II and the final layered phase (*P*-4m2). The intermediate states in experiment with different polymeric concentrations might be more complex than this simple representative structure (*P*-42$_1$m).

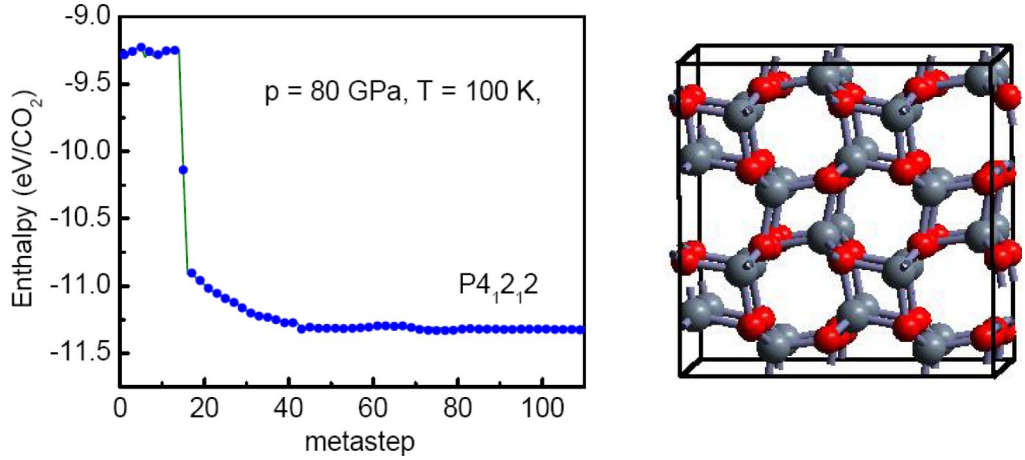

Fig. S2. Enthalpy evolution for metadynamics simulation starting from Phase III (*Cmca*) at 80 GPa and 100 K, with 32 CO_2 molecules. Slightly larger Gaussian parameters [width 7 (kbar·Å^3)$^{1/2}$ and height (50 kbar·Å^3)] are used in this simulation, resulting in a rapid transition. Right inset is the supercell of the final $P4_12_12$ structure looked along [001] direction.