

## **Supporting Information**

### **Effect of Small Cage Guests on Dissociation Properties of Tetrahydrofuran Hydrates**

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Table S1. The experimental results of eutectic temperatures and dissociation temperatures of THF hydrates pressurized by helium at various THF concentrations in liquid phase.<sup>a</sup>

Helium Pressure (MPa)	THF concentration (mol%)									
	2.86	4.23	5.56	6.85	8.11					
Eutectic temperature (K)					Dissociation temperature of hydrate (K)					
0.1013	272.2	272.2	272.0	b	b	276.9	278.1	278.7	278.6	278.5
5.00	-	-	272.0	b	b	-	-	279.5	279.4	279.5
10.00	271.7	271.6	271.6	b	b	277.5	279.3	279.7	279.6	279.3
15.00	-	-	271.3	-	-	-	-	280.0	-	-
20.00	271.2	271.1	270.9	b	b	277.6	279.5	280.4	280.0	279.8
25.00	-	-	270.5	-	-	-	-	280.6	-	-
30.00	270.5	270.4	270.3	b	b	278.3	280.2	280.8	280.7	280.4
35.00	-	-	269.9	-	-	-	-	281.0	-	-

<sup>a</sup> The dissociation temperature at each pressure was measured at least 3 times by the HPμDSC. Standard uncertainties *u* are *u*(*T*) = 0.1 K and *u*(*P*) = 0.005 MP

<sup>b</sup> There is no eutectic temperature detected during the heating step in this system.

Table S2. The experimental results of dissociation temperatures of the THF-methane mixed hydrates at various THF concentrations and at pressures ranging from 5.00 to 35.00 MPa.<sup>a</sup>

Methane Pressure (MPa)	THF Concentration (wt%)						
	1.0	2.5	5.0	10.0	19.1	22.7	26.1
THF Concentration (mol%)							
	0.25	0.64	1.30	2.70	5.56	6.85	8.11
Dissociation temperature (K)							
5.00	290.6	294.5	297.2	299.2	301.0	300.7	300.5
10.00	296.1	299.4	302.3	303.3	305.7	305.7	305.1
15.00	298.4	301.7	304.9	306.7	-	-	-
20.00	299.7	303.7	306.4	308.1	310.3	310.3	310.2
25.00	300.5	305.0	307.5	309.4	-	-	-
30.00	301.1	305.9	308.4	310.1	312.8	312.7	312.7
35.00	301.9	306.6	309.1	310.7	-	-	-

<sup>a</sup> Standard uncertainties  $u$  are  $u(T) = 0.1$  K and  $u(P) = 0.005$  MPa

Table S3. Lennard-Jones potential for helium and methane used in the MD simulation

	$\sigma$ (nm)	$\epsilon$ (kJ/mol)
<b>Helium</b>	0.2556	0.08368
<b>Methane (C)</b>	0.3500	0.27614
<b>Methane (H)</b>	0.2500	0.12552

Table S4. The simulation results of system enthalpy (kJ/mol H<sub>2</sub>O) at pressures ranging from 5 to 30 MPa and at temperature ranging from 300 to 315 K.

System	Phase	T (K)	P (MPa)			
			5.0	10.0	20.0	30.0
Full occupancy of methane in small ( <sup>5</sup> <sup>12</sup> ) cages	Hydrate	300	-50.93±0.01	-50.81±0.02	-50.61±0.03	-50.39±0.02
		305	-50.48±0.01	-50.38±0.00	-50.17±0.01	-49.94±0.01
		310	-50.04±0.02	-49.95±0.01	-49.74±0.01	-49.53±0.01
		315	-49.60±0.01	-49.51±0.00	-49.29±0.00	-49.08±0.01
	Melted	300	-42.50±0.03	-42.40±0.03	-42.20±0.03	-42.03±0.01
		305	-41.81±0.03	-41.74±0.02	-41.54±0.01	-41.35±0.02
		310	-41.13±0.04	-41.10±0.01	-40.88±0.02	-40.70±0.01
		315	-40.52±0.01	-40.40±0.05	-40.23±0.00	-40.04±0.00
	Melted-Hydrate	300	8.43±0.04	8.41±0.01	8.41±0.01	8.36±0.01
		305	8.66±0.03	8.65±0.03	8.64±0.00	8.59±0.03
		310	8.90±0.06	8.85±0.01	8.86±0.02	8.83±0.01
		315	9.08±0.01	9.10±0.05	9.06±0.01	9.04±0.02
Half occupancy of methane in small ( <sup>5</sup> <sup>12</sup> ) cages	Hydrate	300	-51.28±0.00	-51.17±0.01	-50.95±0.01	-50.73±0.01
		305	-50.86±0.01	-50.75±0.00	-50.56±0.01	-50.33±0.02
		310	-50.46±0.01	-50.35±0.01	-50.14±0.01	-49.92±0.01
		315	-50.04±0.01	-49.94±0.01	-49.73±0.01	-49.51±0.01
	Melted	300	-44.73±0.18	-44.80±0.36	-44.60±0.20	-44.50±0.05
		305	-44.11±0.16	-43.93±0.18	-43.91±0.22	-43.59±0.13
		310	-43.30±0.02	-43.30±0.18	-43.10±0.14	-42.84±0.03
		315	-42.65±0.01	-42.59±0.01	-42.41±0.00	-42.20±0.04
	Melted-Hydrate	300	6.55±0.18	6.37±0.37	6.35±0.19	6.23±0.04

		305	$6.75 \pm 0.17$	$6.82 \pm 0.18$	$6.66 \pm 0.22$	$6.74 \pm 0.14$
		310	$7.16 \pm 0.02$	$7.06 \pm 0.18$	$7.04 \pm 0.13$	$7.08 \pm 0.04$
		315	$7.39 \pm 0.00$	$7.35 \pm 0.02$	$7.32 \pm 0.01$	$7.32 \pm 0.05$
	Hydrate	300	$-51.64 \pm 0.00$	$-51.54 \pm 0.02$	$-51.29 \pm 0.03$	$-51.12 \pm 0.01$
		305	$-51.27 \pm 0.01$	$-51.15 \pm 0.01$	$-50.95 \pm 0.00$	$-50.73 \pm 0.01$
		310	$-50.85 \pm 0.03$	$-50.78 \pm 0.00$	$-50.56 \pm 0.02$	$-50.34 \pm 0.01$
		315	$-50.50 \pm 0.02$	$-50.39 \pm 0.01$	$-50.14 \pm 0.01$	$-49.94 \pm 0.03$
Empty occupancy of methane in small ( $5^{12}$ ) cages	Melted	300	$-46.35 \pm 0.01$	$-46.26 \pm 0.01$	$-46.07 \pm 0.01$	$-45.87 \pm 0.01$
		305	$-45.81 \pm 0.00$	$-45.71 \pm 0.01$	$-45.51 \pm 0.00$	$-45.33 \pm 0.00$
		310	$-45.25 \pm 0.00$	$-45.16 \pm 0.00$	$-44.97 \pm 0.00$	$-44.78 \pm 0.01$
		315	$-44.72 \pm 0.01$	$-44.61 \pm 0.02$	$-44.42 \pm 0.01$	$-44.24 \pm 0.00$
	Melted-Hydrate	300	$5.29 \pm 0.01$	$5.27 \pm 0.03$	$5.23 \pm 0.05$	$5.27 \pm 0.02$
		305	$5.45 \pm 0.00$	$5.44 \pm 0.01$	$5.44 \pm 0.01$	$5.42 \pm 0.03$
		310	$5.60 \pm 0.02$	$5.61 \pm 0.03$	$5.59 \pm 0.02$	$5.56 \pm 0.02$
		315	$5.78 \pm 0.03$	$5.78 \pm 0.03$	$5.75 \pm 0.05$	$5.73 \pm 0.08$

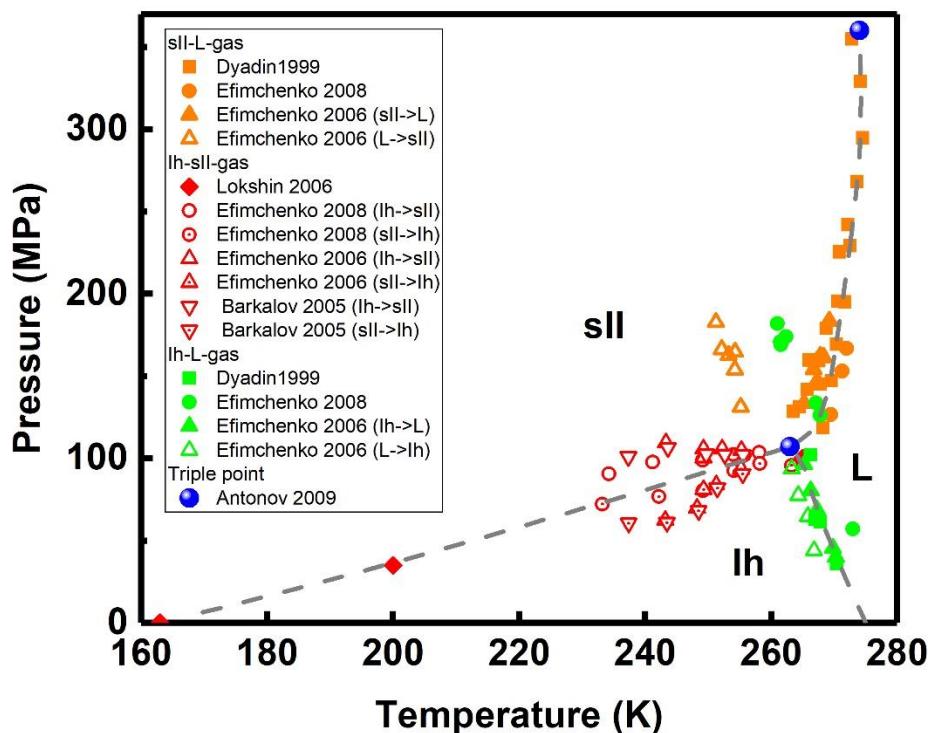
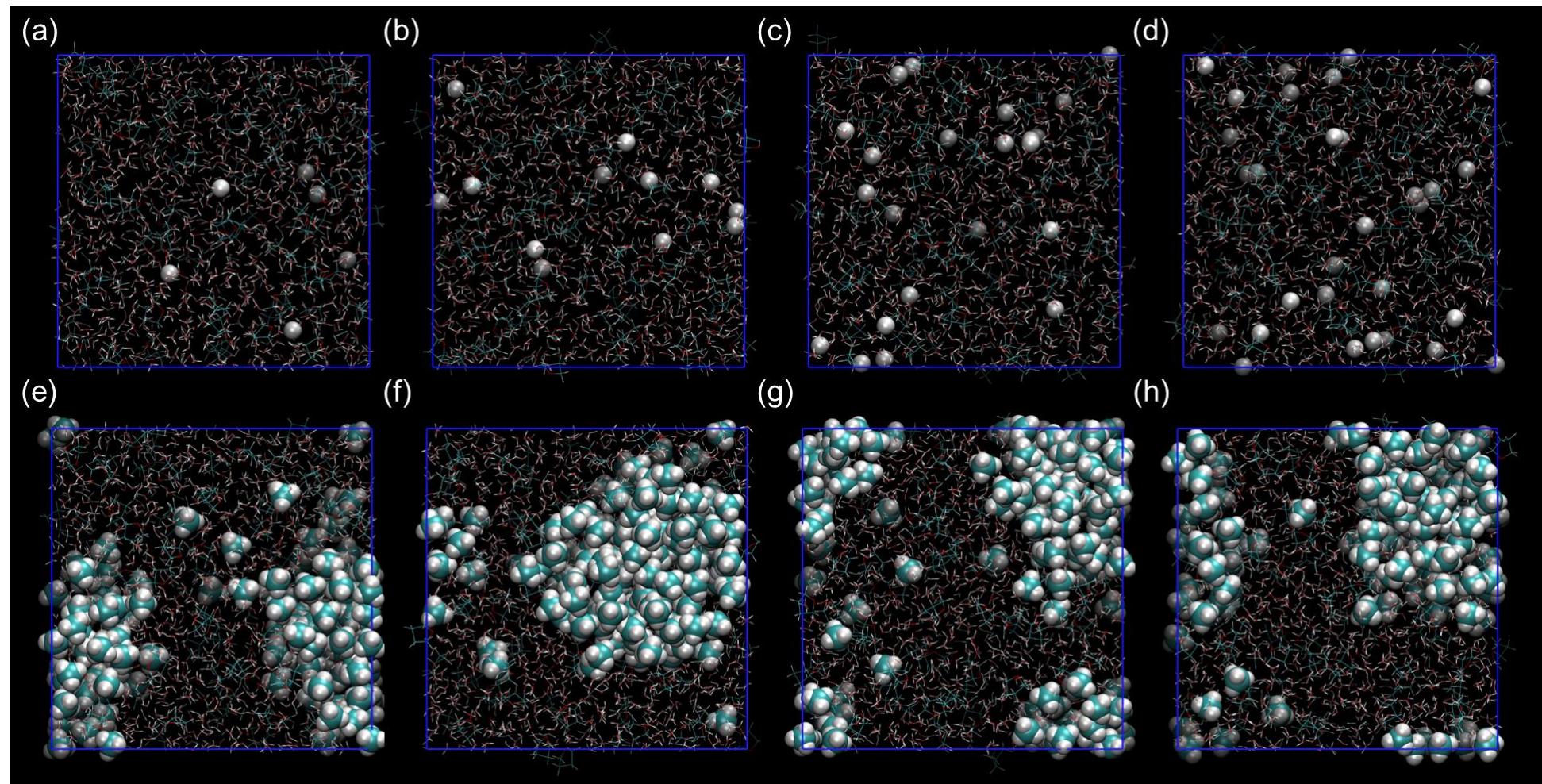


Figure S1. The phase diagram of hydrogen + water system. All the data are adopted from the following references 1-6.

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**Figure S2.** The snapshots of dissociated phases in the MD simulations. The van der Waals type molecules are helium and methane, and the line type molecules are mixtures of THF and water. The pressure and temperature of the dissociated phase of THF-He hydrates are at the dissociating conditions of (a) 5 MPa & 279.5 K, (b) 10 MPa & 279.7 K, (c) 20 MPa & 280.4 K, and (d) 30 MPa & 280.8 K. The pressure and temperature of the dissociated phase of the fully-occupied THF-methane hydrates are (e) 5 MPa & 300 K, (f) 10 MPa & 305 K, (g) 20 MPa & 310 K, and (h) 30 MPa & 315 K.