## Supporting Information for

## Structure-H (sH) Clathrate Hydrate with New Large Molecule Guest

## Substances

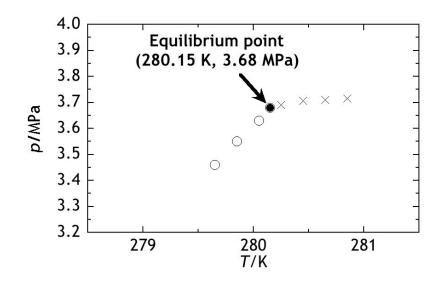
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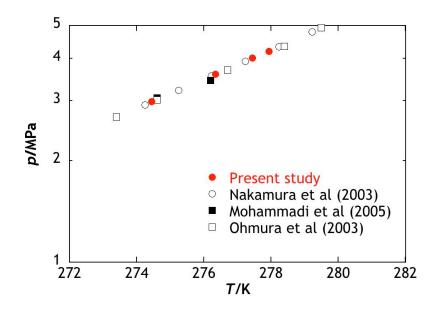


**Supporting Figure S1.** Scheme of determining equilibrium pressure–temperature point in a CH₄–BrCP–water system. ●, Equilibrium point (280.15 K, 3.68 MPa).

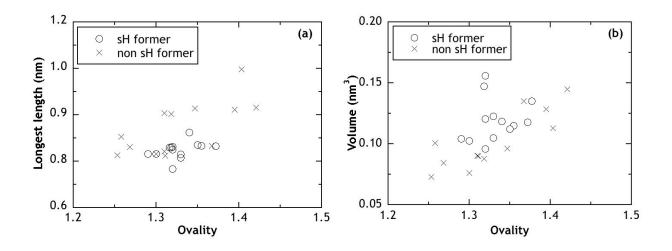
**Supporting Table S1.** Equilibrium pressure–temperature conditions for methane clathrate hydrates in our experimental setup.

$T^{a}/\mathbf{K}$	<i>p<sup>b</sup></i> /MPa
274.5	2.98
276.4	3.59
277.5	4.01
277.9	4.20

*a*: Uncertainty of dissociation temperature was estimated to be  $\pm 0.1$  K with a confidence level of approximately 95 %. *b*: Uncertainties of pressure measurements were estimated to be  $\pm 0.05$  MPa with a confidence level of approximately 95 %.



**Supporting Figure S2.** Equilibrium pressure–temperature conditions of methane clathrate hydrates. •, present study;  $\circ$ , Nakamura *et al.*;<sup>1</sup> •, Mohammadi *et al.*;<sup>2</sup>  $\Box$ , Ohmura *et al.*;<sup>3</sup>



**Supporting Figure S3**. Relationships between geometric properties of large guest with/without sH hydrate formation. sH former: MCH, MCP, NH, isopentane, cycloheptane, adamantine, cis-1,2-dimethyl hexane, pinacolone, cycloheptanone, pinacoly alcohol, tetramethylsilane, TBME, BrCP, BrCH. non sH former: toluene, n-hexane, n-pentane, isoprane, trans-1,2-dimethylhexane, 2,4-dimethylpentane, 3-methyl-1-butene, 2-methyl-2-butene, 2-methyl-1-butene, trans-2-butene, diethyl ether, 2,2,4-trimethylpentane, methyl acetate.

## Reference.

1) Nakamura, T.; Makino, T.; Saguaro, T.; Ohgaki, K. Stability boundaries of gas hydrates helped by methane—structure-H hydrates of methylcyclohexane and cis-1,2-dimethylcyclohexane. *Chem. Eng. Sci.* **2003**, 58, 269–273.

2) Mohammadi, A. H.; Anderson, R.; Tohidi, B. Carbon Monoxide Clathrate Hydrates: Equilibrium Data and Thermodynamic Modeling. *AIChE J.* **2005**, 51, 2825–2833.

3) Ohmura, R.; Uchida, T.; Takeya, S.; Nagao, J.; Managua, H.; Ebinuma, T.; Narita, H. Clathrate hydrate formation in (methane + water + methylcyclohexanone) systems: the first phase equilibrium data. *J. Chem. Thermodyn.* **2003**, 35, 2045–2054.