Supplementary Information

Effect of introducing a cyclobutylmethyl group to an onium cation on the thermodynamic properties of ionic clathrate hydrate

Sakura Azuma,[a] Jin Shimada,[bcd] Katsuhiko Tsunashima,*[e] Takeshi Sugahara,*[bc] Takayuki Hirai [bc]

a. Advanced Engineering Faculty, National Institute of Technology, Wakayama Collage, 77 Noshima, Nada, Gobo, Wakayama 644-0023, Japan

b. Division of Chemical Engineering, Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan

c. Division of Energy and Photochemical Engineering, Research Center for Solar Energy Chemistry, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan

d. Research Fellow of Japan Society for the Promotion of Science, 5-3-1 Kojimachi, Chiyoda-ku, Tokyo 102-0083, Japan

e. Department of Material Science, National Institute of Technology, Wakayama Collage, 77 Noshima, Nada, Gobo, Wakayama 644-0023, Japan

Corresponding Authors

*(K.T.) Tel: +81-738-29-8413. Fax: +81-738-29-8413. E-mail : tsunashima@wakayama-nct.ac.jp.

*(T.S.) Tel and Fax: +81-6-6850-6293. E-mail: sugahara@cheng.es.osaka-u.ac.jp.

NMR characterization of tri-*n*-butyl(cyclobutylmethyl)phosphonium bromide (P444(1c4)-Br) synthesized in the present study.

^{1}H NMR (400.13 MHz in $CDCl_3$), δ 0.90–1.05 (t, 9H, $P^+CH_2(CH_2)_2CH_3$); 1.41–1.67 (m, 12H, $P^+CH_2(CH_2)_2CH_3$); 1.83–2.05 (m, 4H, $P^+CH_2CH(CH)_2CH_2$); 2.15–2.31 (m, 2H, $P^+CH_2CH(CH)_2CH_2$); 2.32–2.53 (m, 6H, $P^+CH_2(CH_2)_2CH_3$); 2.55–2.75 (m, 3H, $P^+CH_2CH(CH)_2CH_2$).

^{13}C NMR (100.62 MHz in $CDCl_3$), δ 13.36 (s, $P^+CH_2CH_2CH_2CH_3$); 18.70–19.03 (d, $P^+CH_2CH_2CH_2CH_3$); 19.49 (s, $P^+CH_2CH(CH)_2CH_2$); 23.67–23.88 (m, $P^+CH_2CH_2CH_2CH_3$); 25.60 (s, $P^+CH_2CH_2CH_2CH_3$); 26.04 (d, $P^+CH_2CH(CH)_2CH_2$); 29.16-29.22 (d, $P^+CH_2CH(CH)_2CH_2$), 30.17–30.27 (d, $P^+CH_2CH(CH)_2CH_2$).

^{31}P NMR (161.97 MHz in $CDCl_3$), δ 32.04 (s, $P^+(C_4H_9)_3(CH_2CH(CH)_2CH_2)$).

Raman spectra of tri-*n*-butyl(cyclobutylmethyl)phosphonium bromide (P444(1c4)-Br) salt.

Figure S1 shows the Raman spectra of P444(1c4)-Br and P4444-Br salts. As noted in Figure 5, there are some differences derived from cyclobutylmethyl group, but no significant difference exists in the other peaks.

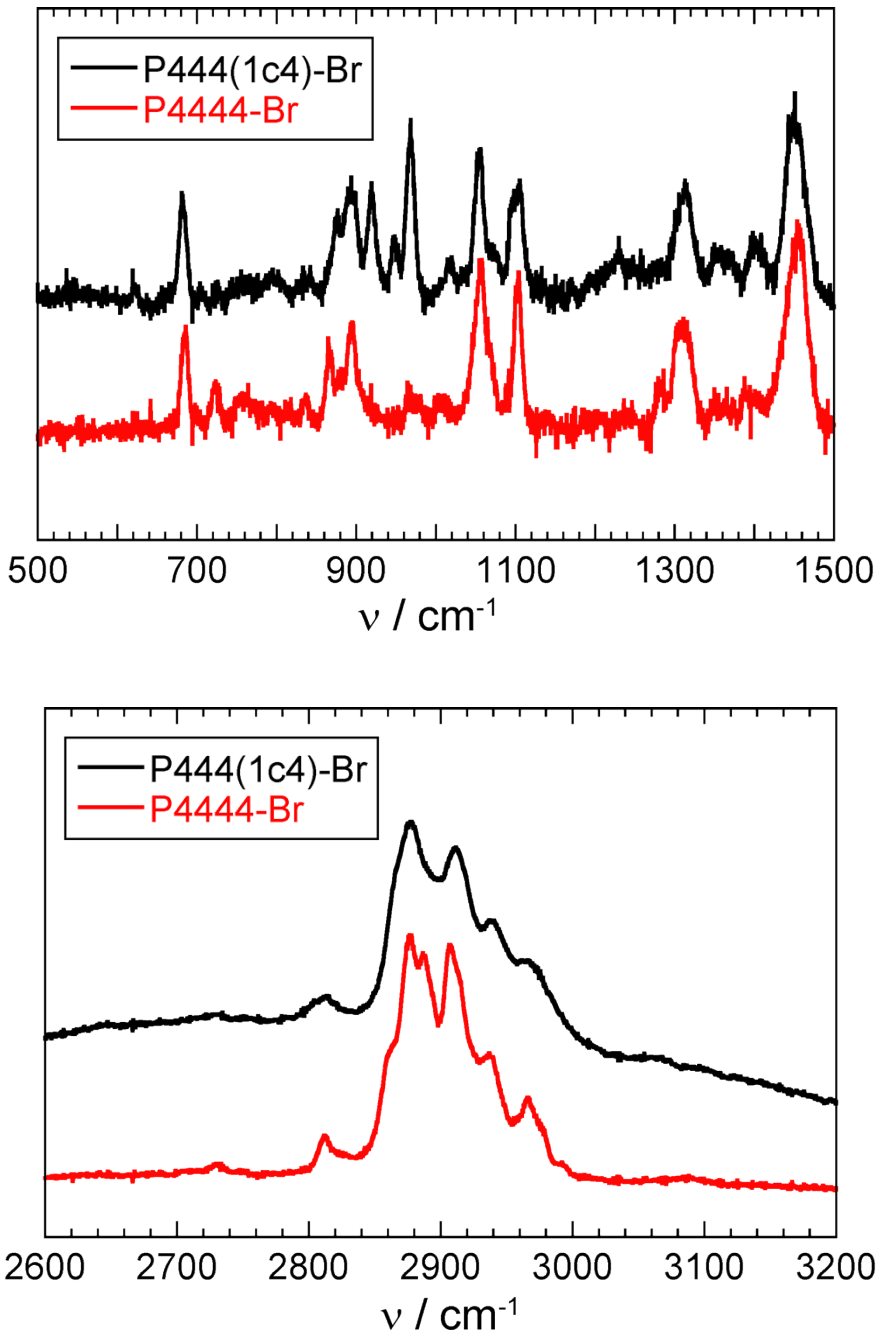

Figure S1. Raman spectra of P444(1c4)-Br and P4444-Br salts recorded at 77 K.