Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
This journal is © the Owner Societies 2022

Supplementary Information for:

Design of structure and relevant properties of semiclathrate hydrates by partly asymmetric alkylammonium salts

Sanehiro Muromachi,*[a] Masato Kida,[b] Masato Morimoto,[c] Shogo Yamane,[d] and Satoshi Takeya[e]

a. Energy Process Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba, 305-8569, Japan.

b. Faculty of Engineering, Kitami Institute of Technology, 165 Koen-cho, Kitami 090-8507, Hokkaido, Japan.

c. Research Institute for Sustainable Chemistry, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

d. National Metrology Institute of Japan (NMIJ), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, 305-8565, Japan.

* Author to whom correspondence should be addressed. (S. M.)

E-mail: s-muromachi@aist.go.jp

Tell: +81-29-861-4287

Fax: +81-29-861-8706

1. Melting temperature data

Table S1. Melting temperature data in the system of $N_{3444}Br$ where x, w, n_w, T_{eq} and U denote mole fraction of salt, mass fraction of salt, molar ratio of water to salt, melting temperature and uncertainty with 95% reliability.

x	$U(x)$	w	n_W	T_{eq} /K
0.0033	0.0004	0.054	299	272.5
0.0066	0.0004	0.102	150	271.9
0.0099	0.0004	0.146	99.9	271.4
0.0123	0.0004	0.176	80.2	270.9
0.0141	0.0004	0.197	70.0	270.5
0.0164	0.0004	0.222	59.8	270.8
0.0197	0.0004	0.255	49.9	271.9
0.0233	0.0005	0.290	41.8	272.5
0.0257	0.0005	0.311	37.9	272.9
0.0287	0.0005	0.336	33.8	273.4
0.0304	0.0005	0.349	31.9	273.5
0.0323	0.0005	0.364	29.9	273.7
0.0345	0.0006	0.379	28.0	273.7
0.0370	0.0006	0.397	26.0	273.8
0.0402	0.0006	0.418	23.9	273.8
0.0477	0.0007	0.462	20.0	273.7
0.0625	0.0009	0.533	15.0	272.7
0.0910	0.0014	0.632	10.0	270.5

Table S2. Melting temperature data in the system of $N_{4445}Br$ where x, w, n_w, T_{eq} and U denote mole fraction of salt, mass fraction of salt, molar ratio of water to salt, melting temperature and uncertainty with 95% reliability.

x	$U(x)$	w	n_W	T_{eq} /K
0.0036	0.001	0.063	277	275.0
0.0069	0.001	0.115	143	277.9
0.0108	0.001	0.169	91.9	279.5
0.017	0.002	0.24	59.0	280.7
0.019	0.002	0.27	50.7	280.8
0.022	0.002	0.29	45.1	280.9
0.024	0.002	0.32	40.1	280.9
0.030	0.002	0.37	32.2	280.9
0.034	0.002	0.40	28.0	280.8
0.044	0.002	0.46	21.5	280.7
0.057	0.002	0.53	16.6	280.2

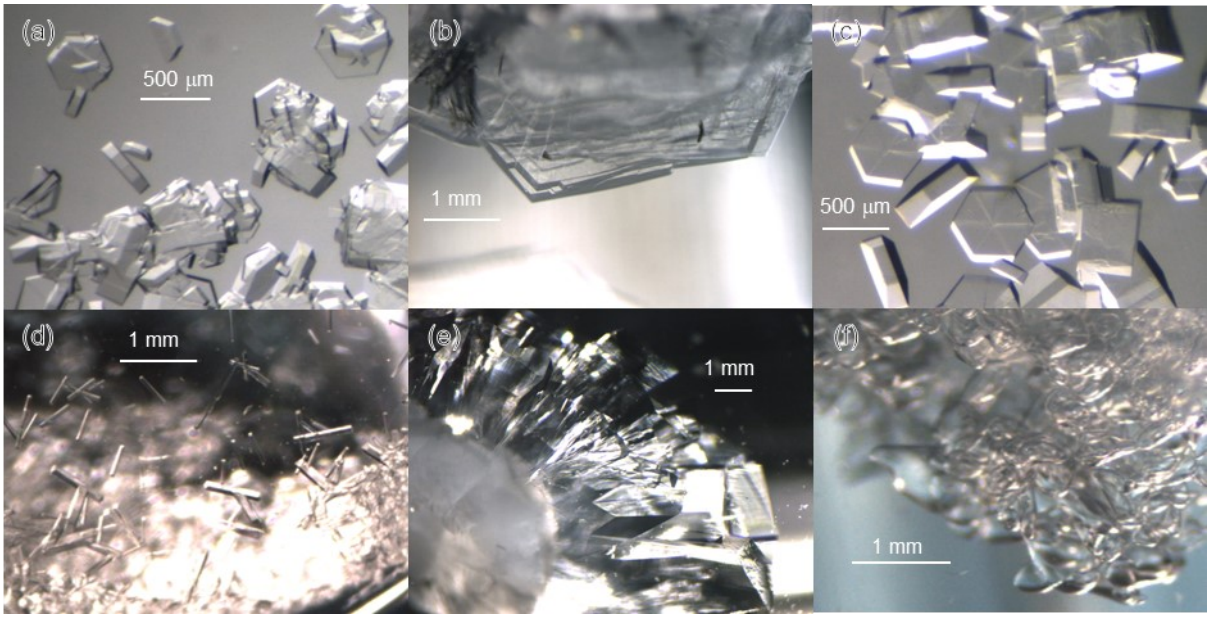
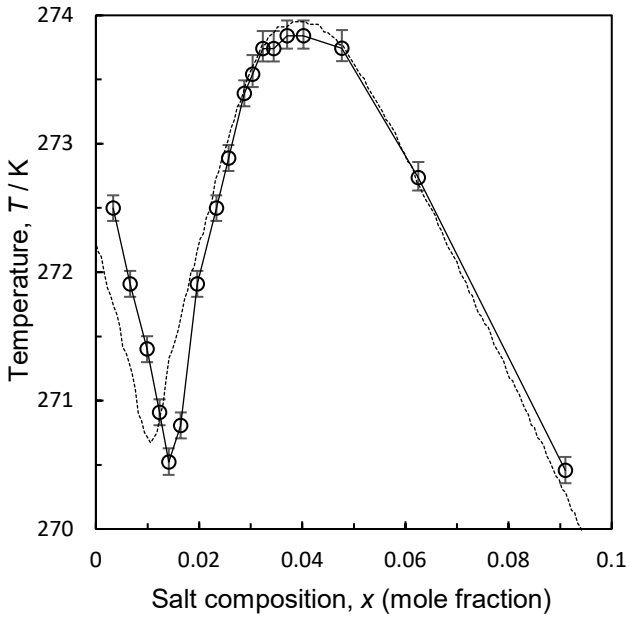
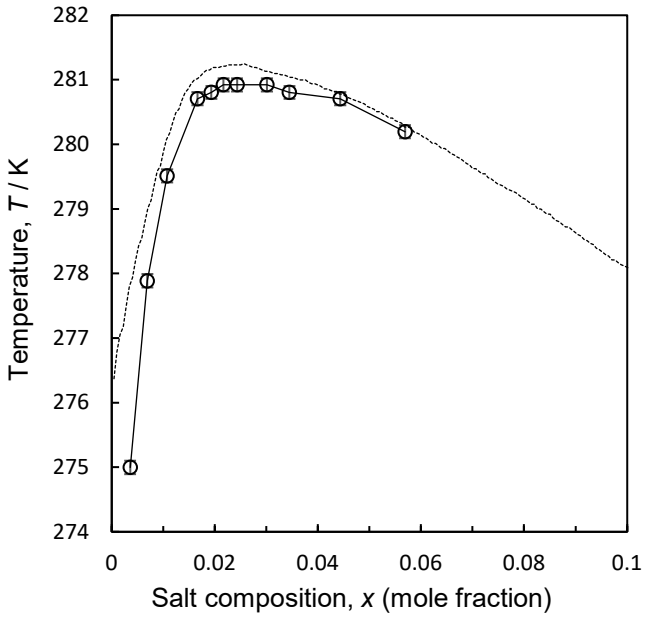


Fig. S1. Pictures of the crystals obtained in this study. (a) $N_{4445}Br$ hydrate at x = 0. 0108 (b) $N_{4445}Br$ hydrate at x = 0.0251 (c) $N_{4445}Br$ hydrate at x = 0.057 (d) $N_{3444}Br$ hydrate at x = 0.0257 (e) $N_{3444}Br$ hydrate at x = 0.0197 (f) $N_{3444}Br$ hydrate at x = 0.0099 (likely ice).



(a) $N_{3444}Br$ hydrate



(b) $N_{4445}Br$ hydrate

Fig. S2 *T*-*x* curves for the present semiclathrate hydrates. The dotted lines show traces of the literature data[37] which are only provided as figures without reporting values.

2. XRD data

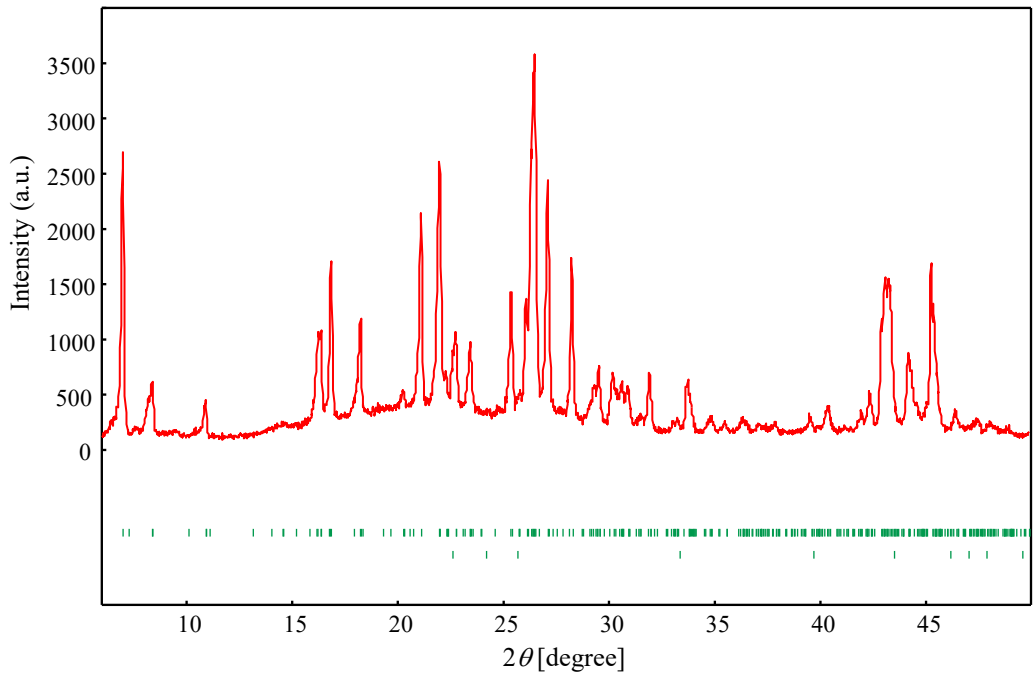


Fig. S3 PXRD pattern for $N_{4445}Br$ hydrate at 93 K.

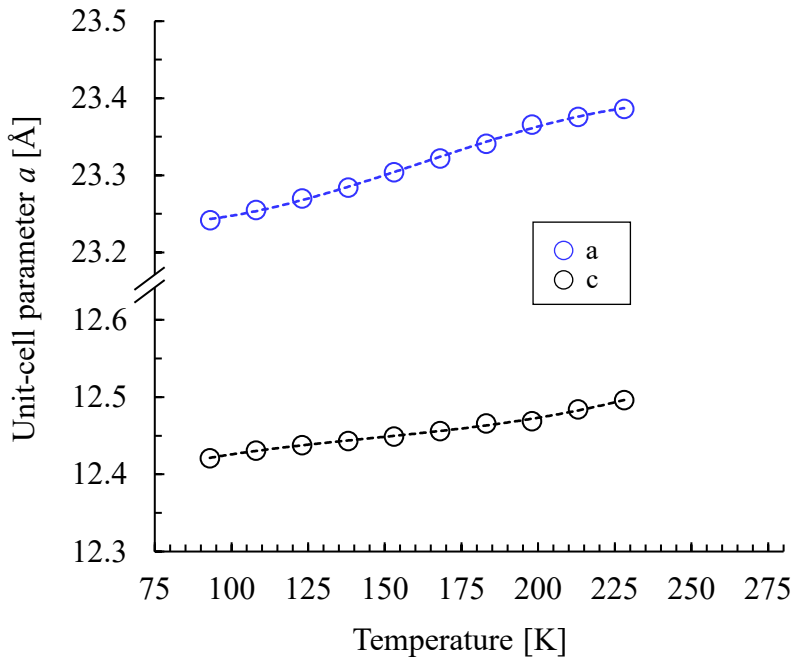
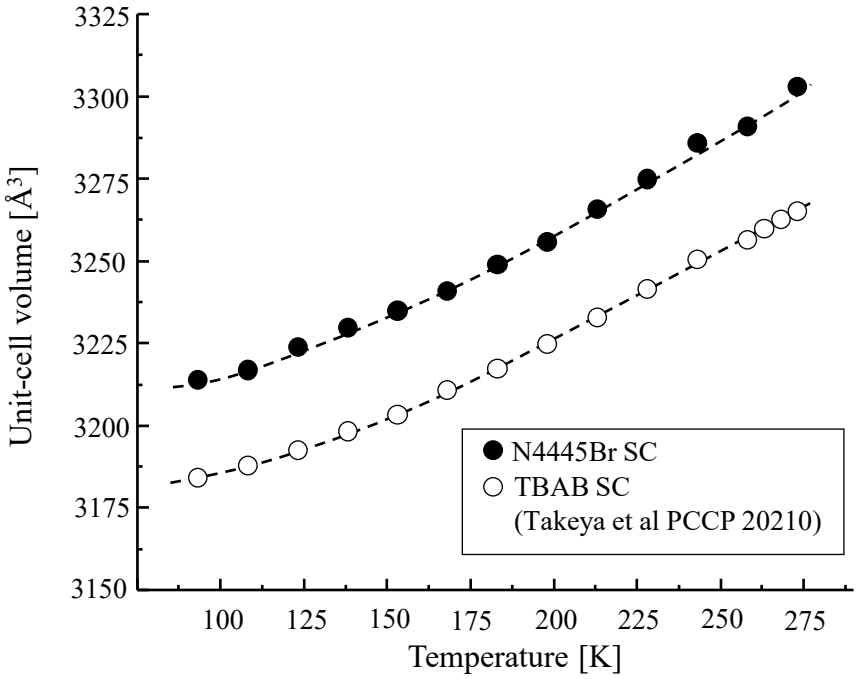
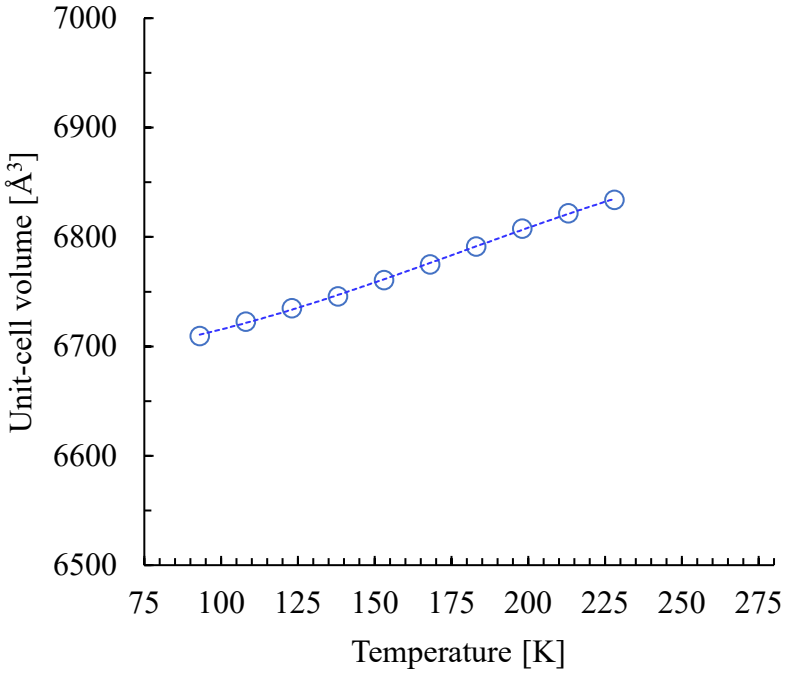


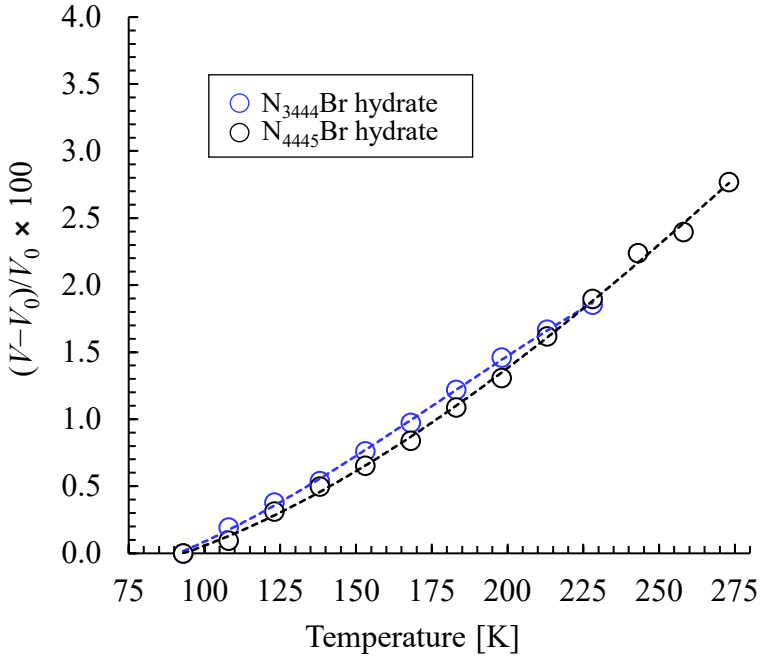
Fig. S4 Unit cell parameters of $N_{3444}Br$ hydrate at temperatures between 93–273 K.



(a) $N_{4445}Br$ hydrate



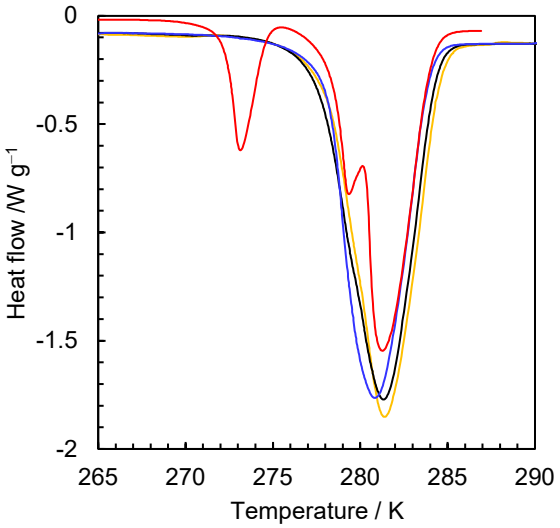
(b) $N_{3444}Br$ hydrate



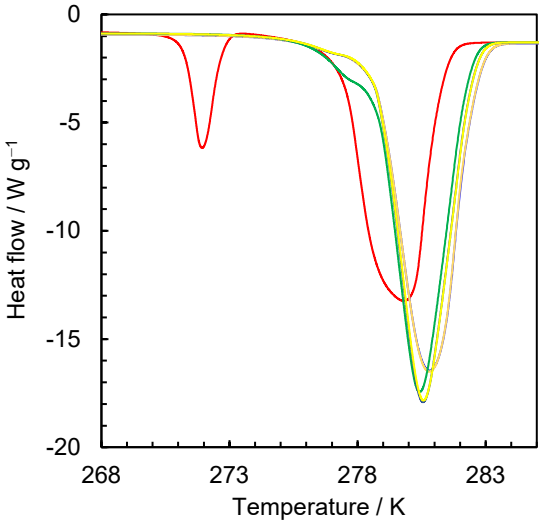
(c) Expansion ratio of unit-cell volume.

Fig. S5 Temperature dependence of unit cell volume measured by PXRD. In figure (c), V and V_0 denote unit-cell volume at a measured temperature and that at 93 K, respectively.

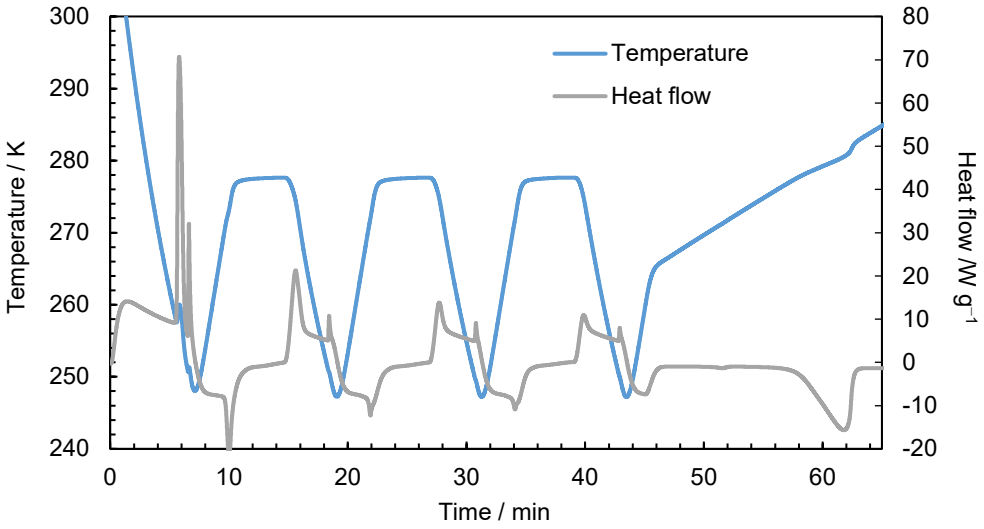
3. DSC data



(a) $N_{3444}Br$ hydrate, $x = 0.0370$.



(b) $N_{4445}Br$ hydrate, $x = 0.0252$.



(c) A typical measurement program.

Fig. S6 DSC curves for the present semiclathrate hydrates. Colours: red, data with quenched sample (without annealing); others, data with annealed sample.

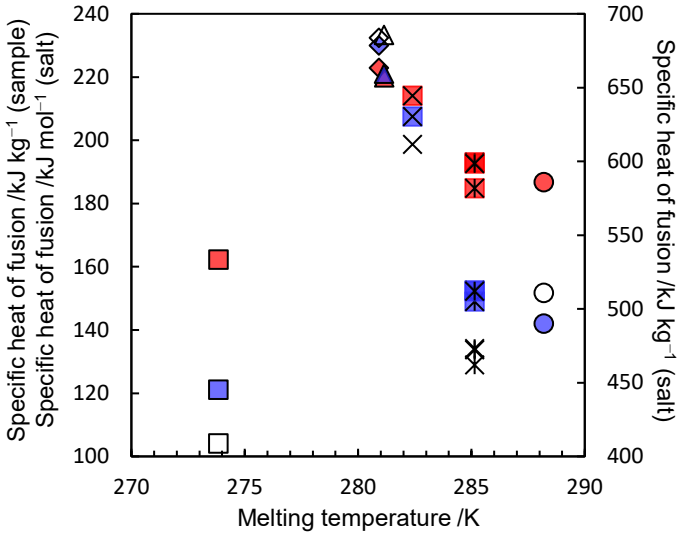


Fig. S7 Specific heats of fusion for semiclathrates. Colours: Red, specific heat of fusion per mass of sample; Blue, specific heat of fusion per mole of salt; Blank, Specific heat of fusion per mass of salt. Symbols for salt: □, $N_{3444}Br$; ◊, $N_{4445}Br$; △,$N_{4444}Br$; ×, $P_{4444}Br$; *, $N_{4444}Br$; ○, $N_{4444}Cl$. See Table S3 for reference data.

Table S3. Reference data for DSC results.

Salt	Reference	Fusion heat					w	T_{eq}	Ref for T_{eq}
		kJ/kg(sample)	kJ/mol(salt)	kJ/mol(water)	kJ/kg(salt)	kJ/kg(water)	in mass frac	K	
$N_{3444}Br$	This work	162	121.1	4.8	408.7	269.1	0.40	273.8	This work
$N_{4445}Br$	This work	223	230.0	6.0	683.7	330.7	0.33	280.9	This work
$N_{4444}Br$ (TBAB)	53	184.8	148.9	5.5	462.0	308.0	0.40	285.2	7 (At 40 mass%)
	11	193	152.5	5.9	473.0	326.0	0.41	285.2	7 (At 40mass%)
	54	192.6	152.2	5.9	472.1	325.3	0.41	285.2	7 (At 40mass%)
	55	219.9	221.0	5.8	685.7	323.7	0.15*	281.2	7 (At 15mass%)
$N_{4444}Cl$ (TBAC)	53	186.7	142.0	5.3	510.8	294.2	0.37	288.2	9
$P_{4444}Br$ (TBPB)	8	214	207.5	5.9	611.4	329.2	0.35	282.4	8

* The crystal sample subjected to DSC was grown in an aqueous solution with 0.15 of the salt in mass fraction.

4. NMR data

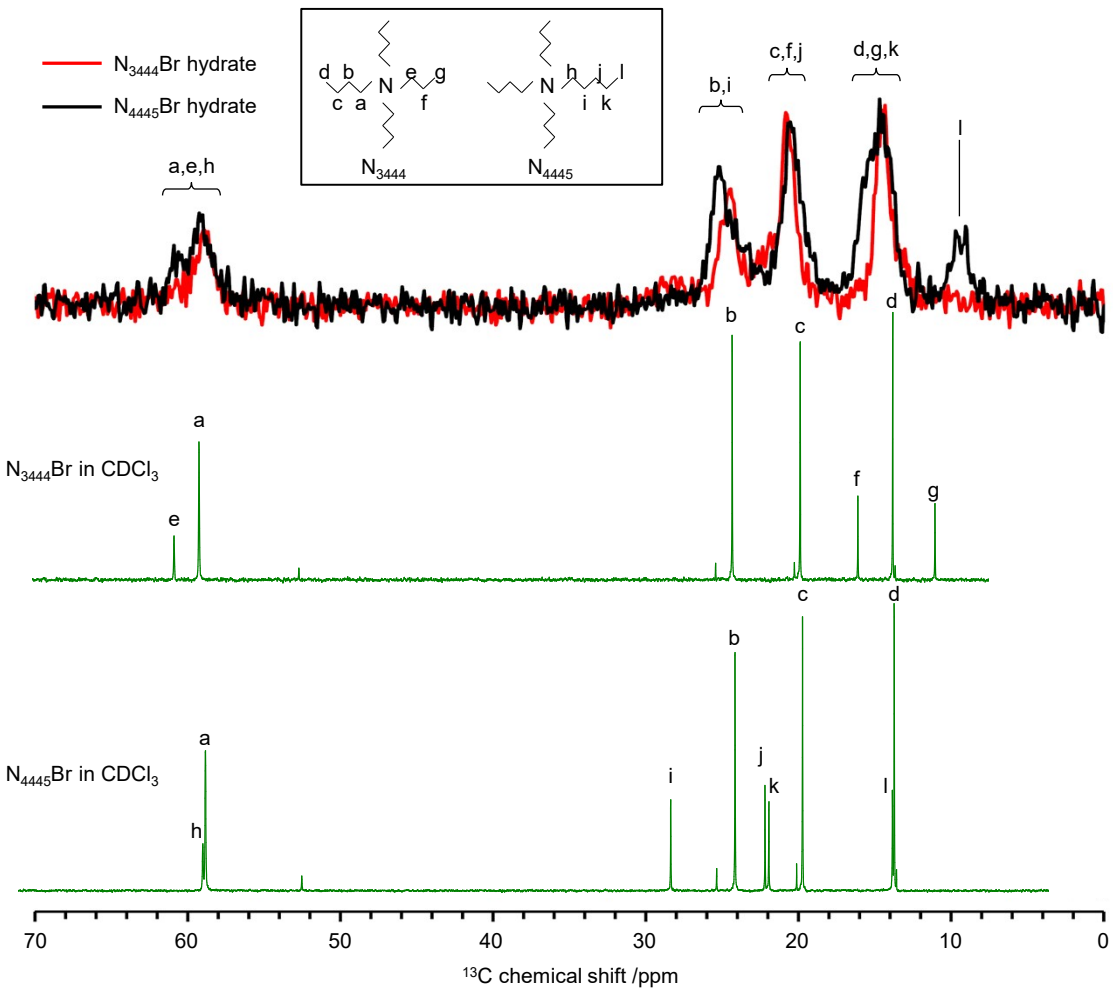


Fig. S8 Solid-state ^{13}C NMR data for the present semiclathrate hydrates of $N_{3444}Br$ and $N_{4445}Br$ and solution-state ^{13}C NMR data of these salts in $CDCl_3$.