

**Supplementary Information for:**

**Guest size effects on a robust structure of semiclathrate hydrates and  
their thermophysical properties**

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Table 1. Melting temperature data for N3444Cl hydrate.

$x$	$U(x)$	$w$	$N_w$	$T/K$
0.0029	0.0015	0.040	349	272.46
0.0073	0.0016	0.097	137	271.88
0.0101	0.0016	0.130	97.7	271.07
0.0123	0.0017	0.154	80.4	270.97
0.0138	0.0017	0.170	71.5	271.74
0.0160	0.0017	0.192	61.5	272.73
0.0186	0.0018	0.217	52.8	273.80
0.0226	0.0018	0.253	43.3	274.68
0.0247	0.0019	0.271	39.5	275.19
0.0267	0.0019	0.287	36.5	275.30
0.0282	0.0019	0.299	34.4	275.50
0.0304	0.0020	0.315	31.9	275.58
0.0325	0.0020	0.330	29.8	275.77
0.0360	0.0021	0.354	26.8	275.77
0.0375	0.0021	0.364	25.6	275.67
0.0445	0.0022	0.405	21.5	275.18
0.0578	0.0025	0.473	16.3	273.69
0.0847	0.0029	0.576	10.8	269.38

Table 2. Melting temperature data for N4445Cl hydrate.

$x$	$U(x)$	$w$	$N_w$	$T/K$
0.0034	0.0013	0.052	297	273.91
0.0065	0.0014	0.096	152	277.27
0.0101	0.0015	0.142	98.2	279.03
0.0125	0.0015	0.171	78.8	279.94
0.0140	0.0015	0.187	70.6	280.35
0.0161	0.0016	0.210	61.1	280.70
0.0194	0.0016	0.242	50.7	281.02
0.0229	0.0017	0.275	42.7	281.54
0.0266	0.0018	0.307	36.6	281.65
0.0292	0.0018	0.328	33.3	281.82
0.0298	0.0018	0.332	32.6	281.82
0.0320	0.0019	0.349	30.3	281.82
0.0340	0.0019	0.363	28.4	281.82
0.0368	0.0019	0.382	26.2	281.65
0.0400	0.0020	0.403	24.0	281.56
0.0473	0.0021	0.446	20.2	281.15
0.0616	0.0024	0.515	15.2	279.94
0.0899	0.0028	0.615	10.1	276.89

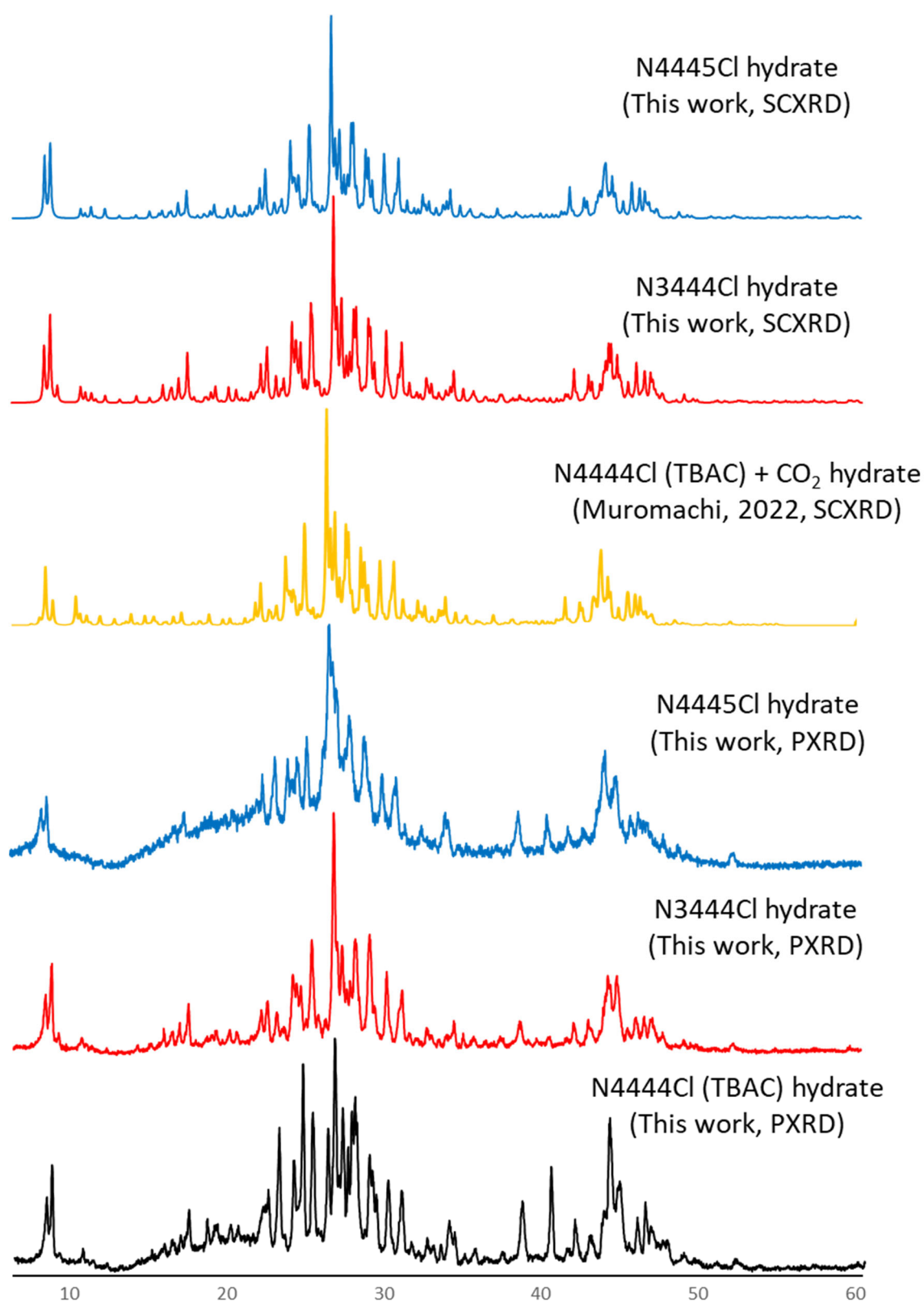


Fig. S1. Powder X-ray diffraction patterns for N4445Cl, N3444Cl and N4444Cl (TBAC) hydrates. Powder patterns generated from SCXRD data were together shown.

Table S3. Comparison of thermal properties between the semiclathrate hydrates which are identified to be the main three structures.

Ionic guest	Hydration number ( $N_w$ )	Reference	Lattice	Space group	Reference	Jeffrey's type	Melting temperature /K	Reference	Fusion heat /kJ kg <sup>-1</sup>	Reference	Fusion heat /kJ mol <sup>-1</sup> (1 salt + $N_w$ of water)
TBA Acetate	25.8	70	cubic	<i>Im3m</i>	70	I	287.8	70	–	–	–
TBA Butyrate	31.7	70	cubic	<i>Pm/3n</i>	70	I	289.9	70	210	70	189.1
TBAF	29.7	7	cubic	<i>I-43d</i>	7	I	301.0	7	222.9	72	177.5
TBA Propionate	27	8	cubic	<i>I-43d</i>	8	I	290.0	–	–	–	–
TBA Propionate	26.8	70	cubic	<i>I-43d</i>	70	I	290.0	8	196	70	156.5
TBPOH	29.6	29	cubic	<i>I-43d</i>	29	I	290.2	29	–	–	–
N3444Cl	26.8	This work	tetragonal	<i>P4<sub>2</sub>/m</i>	This work	III	275.8	This work	166.5	This work	124.2
N4445Cl	32.6	This work	tetragonal	<i>P4<sub>2</sub>/m</i>	This work	III	281.8	This work	173.3	This work	152.3
TBA 2-Hydroxybutyrate	30	54	tetragonal	<i>P-4</i>	54	III	285.3	54	177	54	156.8
TBA Acetate	31	70	tetragonal	<i>P4<sub>2</sub>/m</i>	70	III	288.0	70	208	70	178.9
TBAC	32.2	9	tetragonal	<i>P4<sub>2</sub>/m</i>	9	III	288.2	9	208.7	9	179.1
TBAC	29.7	9	tetragonal	<i>P4<sub>2</sub>/m</i>	9	III	288.3	9	193	9	156.9
TBAC	24.5	9	tetragonal	<i>P4<sub>2</sub>/m</i>	9	III	288.1	9	177.8	9	127.9
TBAF	32.8	27	tetragonal	<i>P4<sub>2</sub>/m</i>	27	III	298.1	27	–	–	–
TBAF	32.4	72	tetragonal	<i>P4<sub>2</sub>/m</i>	27	III	300.4	72	240.3	72	203.1
TBA Glycolate	32	56	tetragonal	<i>P-4</i>	56	III	280.9	56	161	56	144
TBA Lactate	29.8	53	tetragonal	<i>P-4</i>	53	III	283.8	53	191	54	166
TBAOH	31.3	73	tetragonal	<i>P4<sub>2</sub>/m</i>	74	IV	300.5	73	200.4	34	164.8
TBA Propionate	31.6	70	tetragonal	<i>P4<sub>2</sub>/m</i>	70	IV	290.5	70	214	70	189.4
N4445Br	38	61	orthorhombic	<i>Pmma</i>	61	IV	280.9	61	223	61	227.7
TBAB	38	5	orthorhombic	<i>Pmma</i>	5	IV	–	–	–	–	–
TBAB	38.1	71	orthorhombic	<i>Pmma</i>	71	IV	282.7	71	217.5	71	219.4
TBA Propionate	37.4	70	orthorhombic	<i>P6/mmm</i>	70	IV	288.0	70	215.7	70	213.4
TBPB	38	28	orthorhombic	<i>Pmma</i>	28	IV	282.7	32	214	62	215.3
Ni5i5i5i5 F <sup>a</sup>	38	75	orthorhombic	<i>Cmmm</i>	75	IV	304	75	–	–	–

<sup>a</sup> tetra-iso-pentylammonium fluoride.