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Supplementary Information for:

Structural CO_2 capture preference of semiclathrate hydrate formed with tetra-*n*-butylammonium chloride

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1. Experimental details

Table S1. Crystal data and structure refinement results for the present crystal.

empirical formula	$C_{16.61}H_{102.08}NClO_{33.04}$
formula weight, g·mol^{-1}	884.24
temperature, K	123 (2)
wavelength, Å	0.71070
crystal system, space group	Tetragonal, $P4_2/m$
unit cell dimensions, Å	a = 23.557(3) b = 23.557(3) c = 12.4259(16)
volume, Å^3	6895.4(19)
Z, calculated density, g·cm^{-3}	5, 1.084
absorption coefficient _mu	0.141
F(000)	2270
crystal size, mm	0.1 × 0.1 × 0.2
θ range for data collection	2.045, 27.682
index ranges	−29 <h< 30 −15 <k< 30 −16 <l< 16
reflections collected/unique	8422/ 5953
completeness to 2θ	0.999
refinement method	F^2 against all reflections
data/restraints/parameters	8422/ 197/ 691
goodness-of-fit on F^2	1.030
final R indices [$I > 2\Sigma(I)$] R_1, wR_2	0.0595, 0.1563
R indices (all data) R_1, wR_2	0.0877, 0.1746

2. Supplementary information for structure

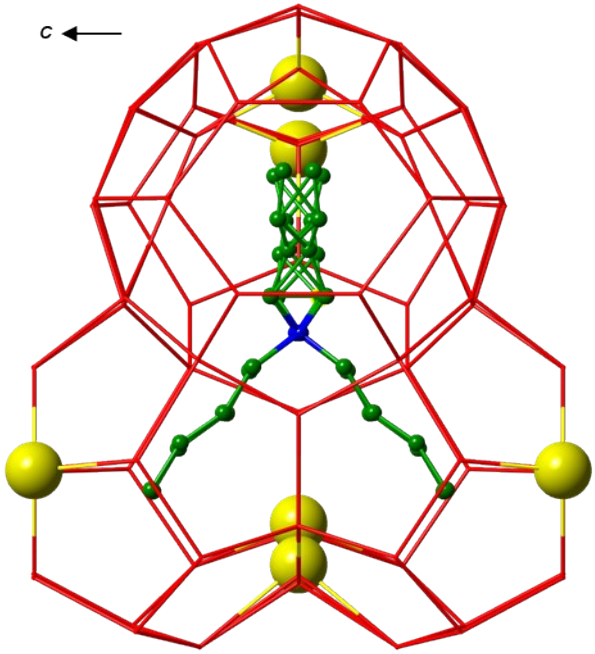

Fig. S1. T^3P cage incorporating TBA cation in the present structure. Coloured spheres: yellow, chlorine; green, carbon of TBA; blue, nitrogen of TBA. Solid red line shows hydrogen bonds between lattice water molecules. Hydrogen atoms are omitted for clarity.

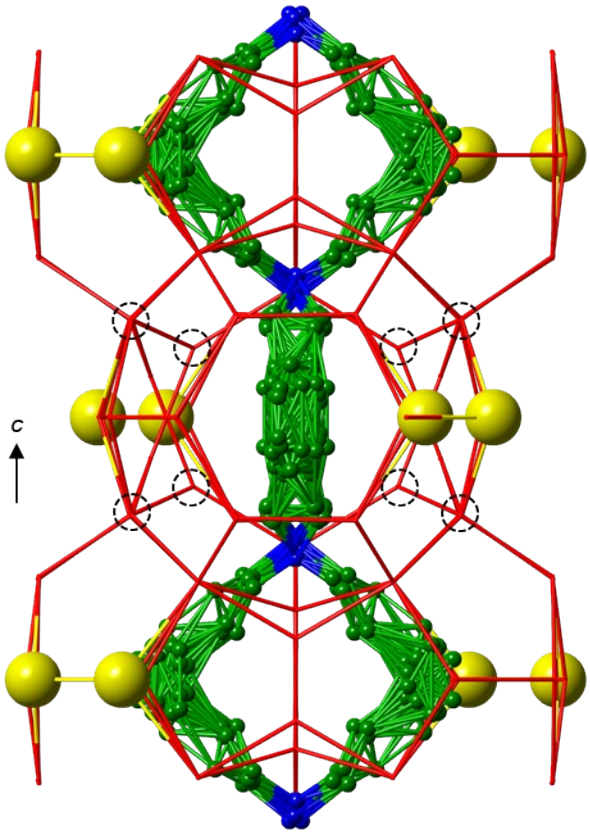

Fig. S2. T^4 cage chain incorporating TBA cation in the present structure. Coloured spheres: yellow, chlorine; green, carbon of TBA; blue, nitrogen of TBA. Solid red line shows hydrogen bonds between lattice water molecules. Hydrogen atoms are omitted for clarity. Nitrogen atoms in TBA and lattice water molecules may alternately switch in order to make T^4 cage chain without vacancy. Due to this switching, eight lattice water molecules (indicated by dotted circle) are also switched.

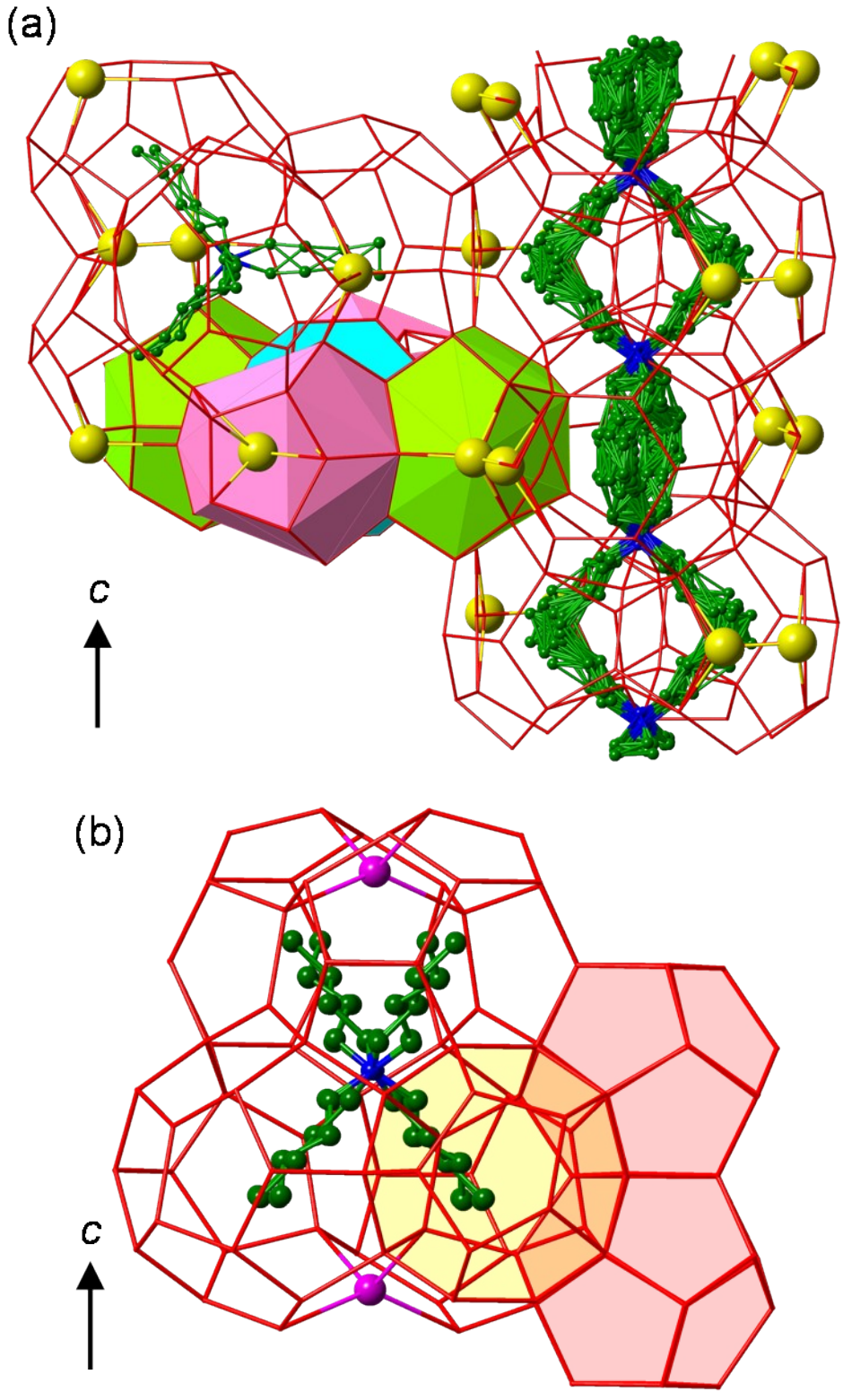

Fig. S3. Cage framework for (a) the present TBAC + CO_2 hydrate and (b) TBAB + CO_2 hydrate [10]. Sphere: Magenta, bromide. Coloured polyhedra: magenta, D_L cage, light green, D_M cage; light blue, D_N cage; Yellow, D_A cage; Red, D_B cage.

Table S2. The shortest distances between chloride anion and nitrogen of TBA cation.

From		To	Distance /Å
N1 in T^3P cage	-	Cl3	5.1097
	-	Cl1	5.4341
	-	Cl2	5.8639
	-	ClD2	6.8776
	-	ClD1	7.0397
N2 in T^4 cage	-	Cl1	6.791
	-	Cl3	7.4891
	-	Cl2	10.1149
	-	ClD1	11.2205
	-	ClD2	13.0971
N22 in T^4 cage	-	Cl1	6.9055
	-	Cl3	7.534
	-	Cl2	10.1718
	-	ClD1	11.3658
	-	ClD2	13.2389