

Electronic Supplementary Information

**Guest replacement in a flexible single-crystal host by mixing
the surrounding gas**

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Contents

Additional adsorption measurement

(Figures S1-S4)

pS2

Additional structural information

(Figures S5-S8, Table S1)

pS5

Reference

pS9

<Additional adsorption isotherm of 1 in various conditions >

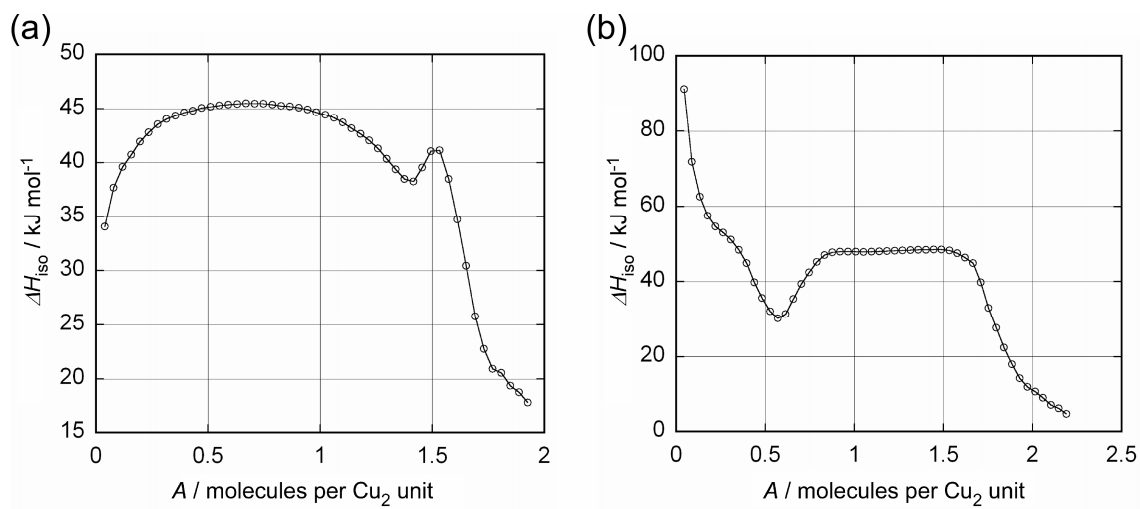


Figure S1 The plot of adsorption heat (ΔH_{180}) (kJ mol^{-1}) versus adsorption amount: (a) methanol, (b) acetonitrile. (A : adsorbed amount of organic vapors in crystal host **1**).

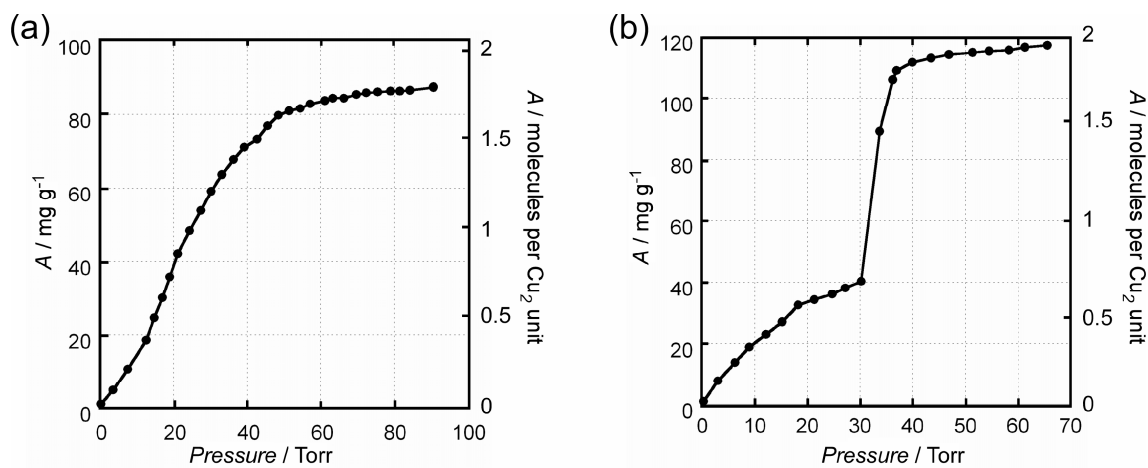


Figure S2 Adsorption isotherm curve for **1** at 293 K: pure methanol (a) and pure acetonitrile (b). (A : adsorbed amount of organic vapors in crystal host **1**).

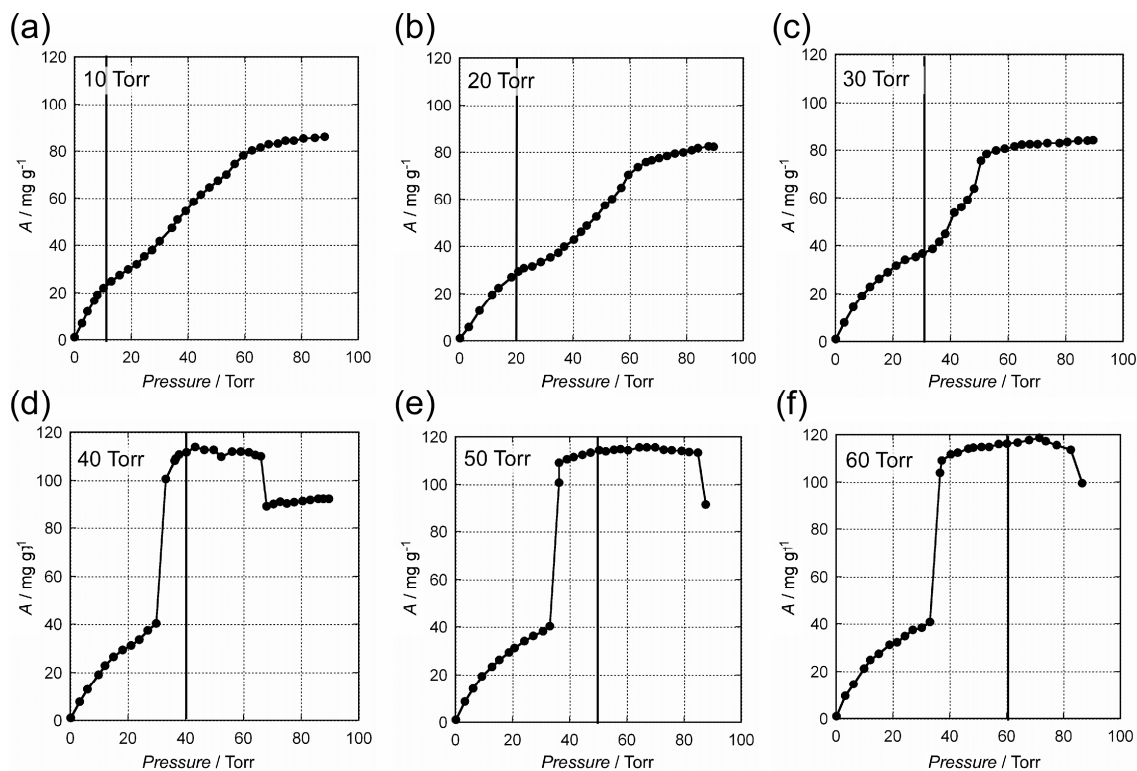
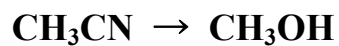


Figure S3 Adsorption isotherm curve of mixture for **1** at 293 K with various switching pressure (10 Torr (a), 20 Torr (b), 30 Torr (c), 40 Torr (d), 50 Torr (e), 60 Torr (f)). (*A*: adsorbed amount of organic vapors in crystal host **1**).

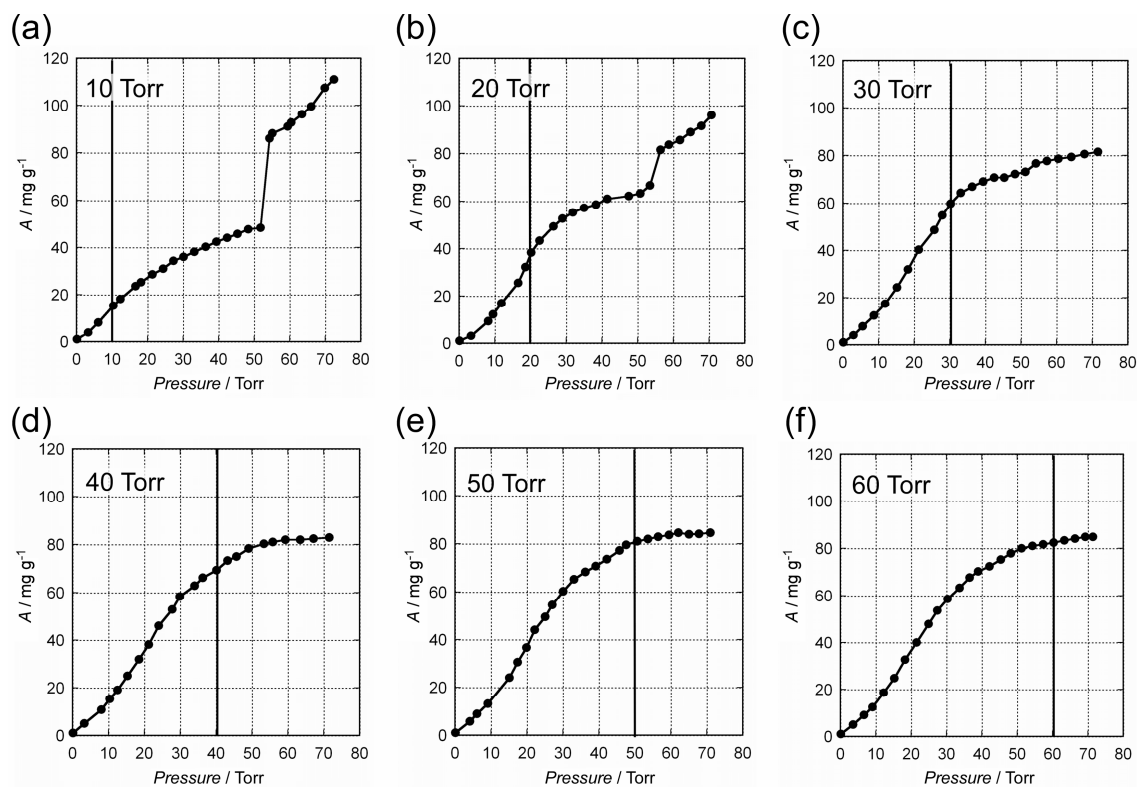
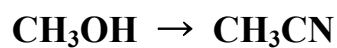


Figure S4 Adsorption isotherm curve of mixture for **1** at 293 K with various switching pressure (10 Torr (a), 20 Torr (b), 30 Torr (c), 40 Torr (d), 50 Torr (e), 60 Torr (f)). (A : adsorbed amount of organic vapors in crystal host **1**).

<Additional structural data for inclusion crystal of 1>

Table S1. Crystallographic data for single-crystal **1** following by various sequential addition of methanol vapor and/or acetonitrile vapor.

Complex	1•2.0 CH ₃ CN	1•0.5 CH ₃ CN•1.3 CH ₃ OH	1•1.6 CH ₃ OH
Condition	CH ₃ CN (70 Torr)	CH ₃ OH (38 Torr, 2.5 h)→CH ₃ CN (70 Torr, 2h)	CH ₃ CN (45 Torr, 11h)→CH ₃ OH (98 Torr, 3.5 h)
Empirical formula	C ₃₆ H ₃₀ Cu ₂ N ₄ O ₈	C _{34.32} H _{30.76} Cu ₂ N _{2.50} O _{8.32}	C _{33.56} H _{30.24} Cu ₂ N ₂ O _{8.56}
Crystal size / mm ³	0.35 × 0.16 × 0.06	0.40 × 0.16 × 0.03	0.55 × 0.14 × 0.05
<i>M</i> / g mol ⁻¹	773.74	754.38	741.56
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>T</i> / K	90	90	90
<i>a</i> / Å	9.674(4)	9.6836(14)	9.6996(16)
<i>b</i> / Å	10.558(4)	10.1691(14)	9.9844(16)
<i>c</i> / Å	10.644(5)	10.6629(16)	10.7765(17)
<i>α</i> / °	84.420(10)	71.897(4)	70.417(3)
<i>β</i> / °	62.980(7)	64.393(3)	65.104(2)
<i>γ</i> / °	63.864(7)	63.142(3)	62.126(2)
<i>V</i> / Å ³ a)	862.2(6)	836.0(2)	824.3(2)
<i>Z</i>	1	1	1
<i>D</i> _{calcd} / g cm ⁻³	1.490	1.495	1.496
<i>μ</i> (Mo-Kα) / mm ⁻¹	1.291	1.330	1.351
Reflections collected	5594	6204	5559
Independent reflections (Rint)	3621 (0.0424)	4092 (0.0307)	3746 (0.0232)
Goodness of fit	1.083	1.037	1.044
<i>R</i> 1 (<i>I</i> > 2σ (all data))	0.0749 (0.0997)	0.0538 (0.0809)	0.0380 (0.0449)
<i>wR</i> 2 (<i>I</i> > 2σ (all data))	0.1922 (0.2032)	0.1247 (0.1360)	0.0953 (0.0991)
Least diff. peak (hole) / e Å ⁻³	1.179 (-1.101)	0.741 (-0.489)	0.673 (-0.463)
Void volume / Å ³ a)	172	152	144

a) *V* / *Z* and void volume of vacant crystal host **1** at *α* phase are 804 Å³ and 115 Å³, respectively, in reference S1.

The crystal structure of methanol inclusion of 1

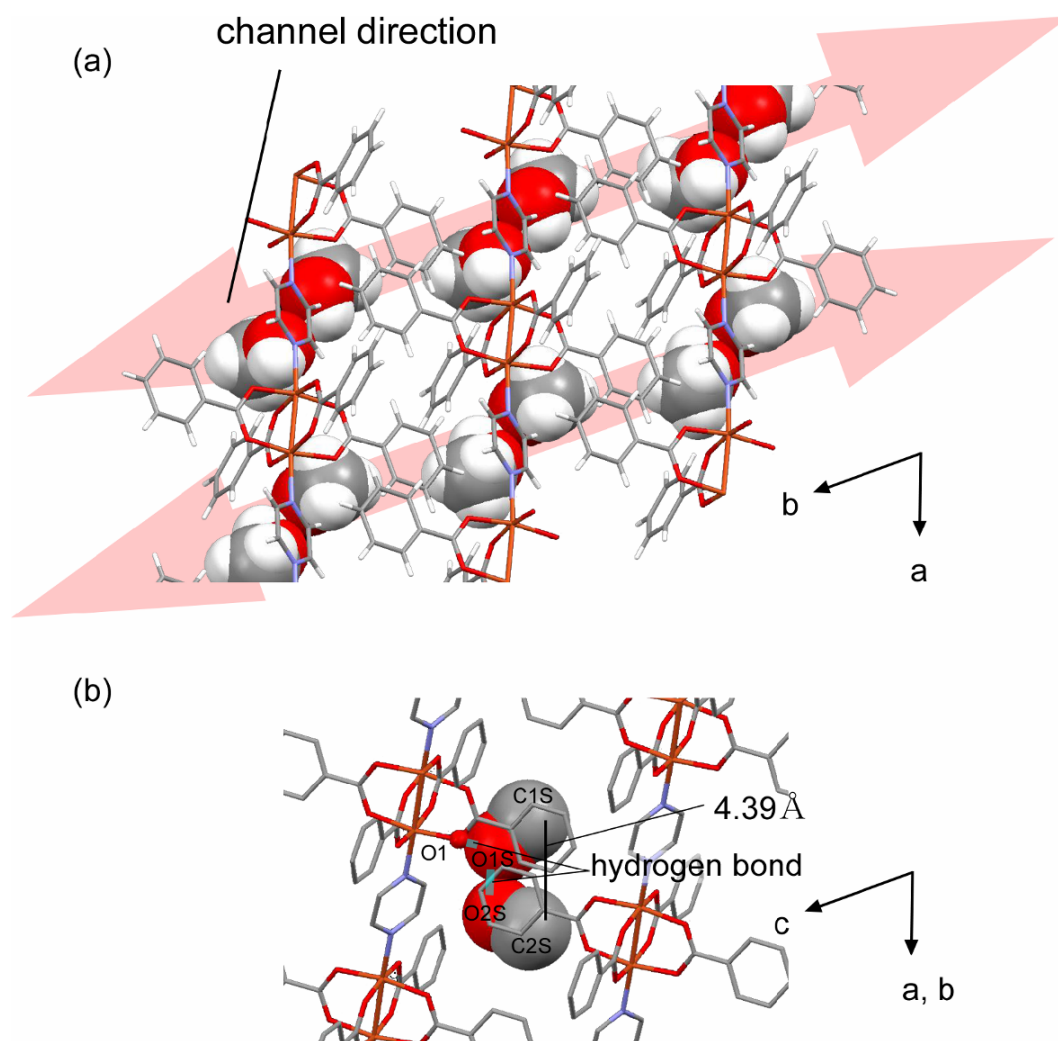
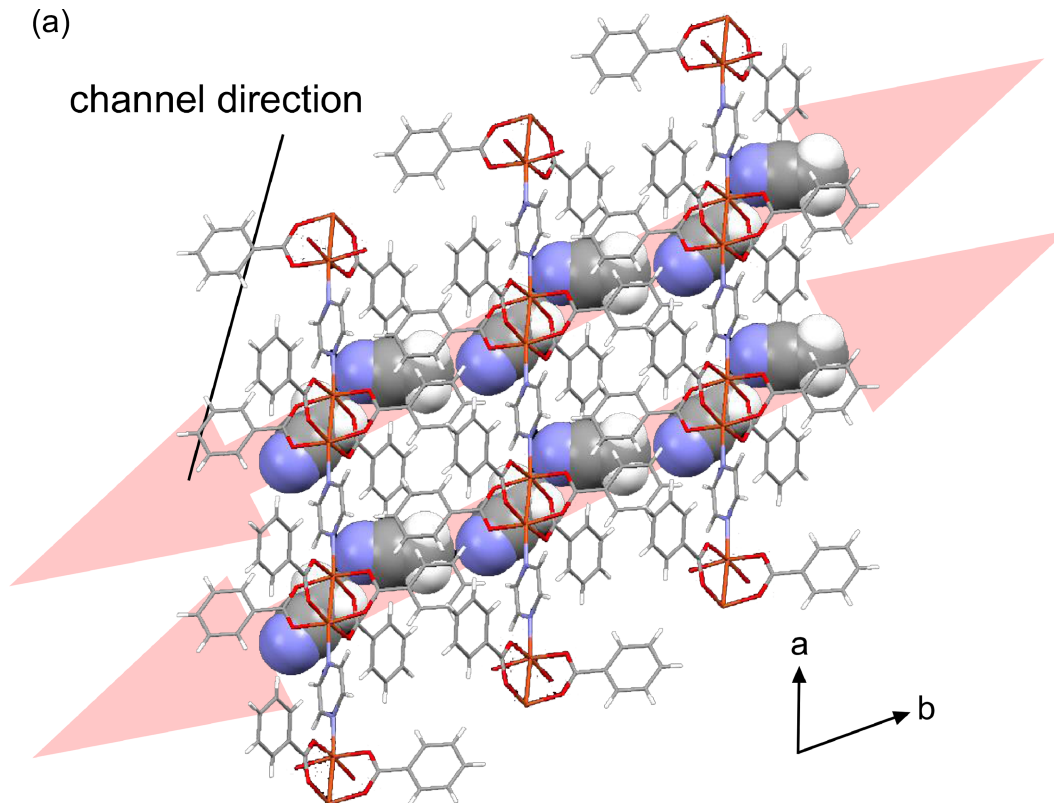


Figure S5 Arrangement of adsorbed methanol in the inclusion crystal of **1** along the channel (a) and the dimer structure of methanol molecules with hydrogen-bonded interaction (b). Disordered molecules and hydrogen atoms are omitted for clarity.

The crystal structure of acetonitrile inclusion of **1**

(a)



(b)

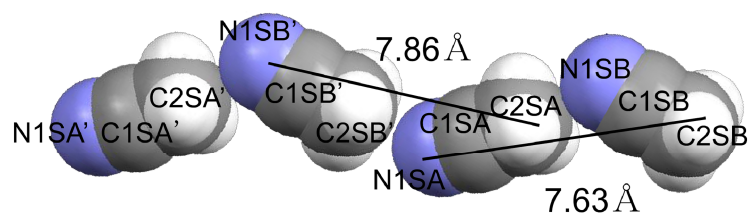


Figure S6 Arrangement of adsorbed acetonitrile in the inclusion crystal of **1** along the channel with the crystal host (a) and arrangement of acetonitrile molecules in the channel (b). Disordered molecules at the centrosymmetry positions are omitted for clarity.

The crystal structure of mixture inclusion which adsorbed both methanol and acetonitrile

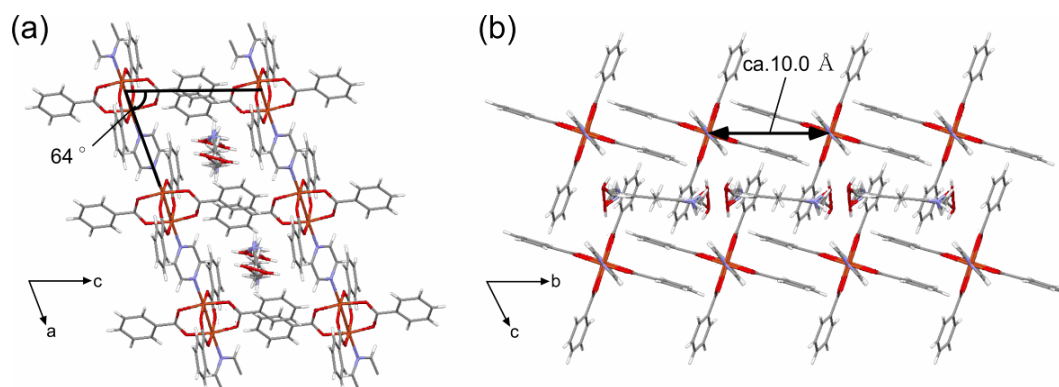


Figure S7 Top view along *b* axis (a) and side view along *a* axis (b) of mixture inclusion crystal of **1** ($1 \cdot 0.5 \text{ CH}_3\text{CN} \cdot 1.3 \text{ CH}_3\text{OH}$): Adsorbed molecules are all array in the channel along *b* axis.

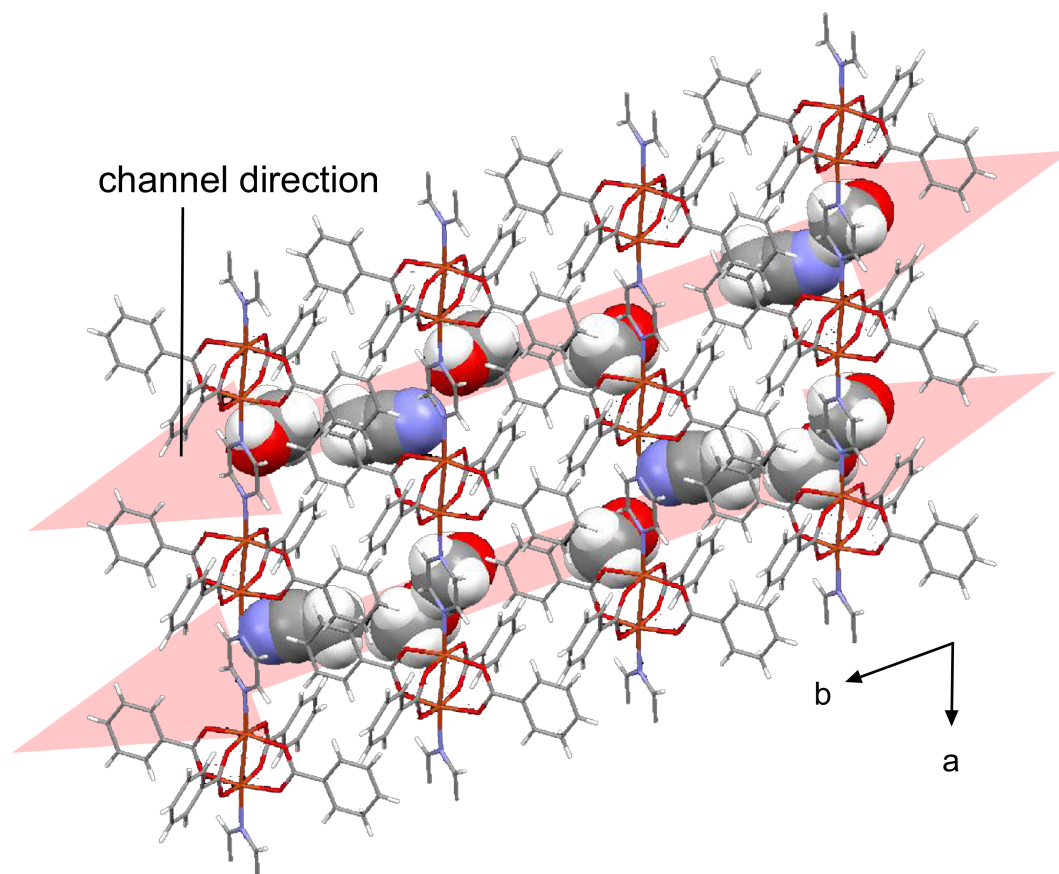


Figure S8 Arrangement of adsorbed methanol and acetonitrile in the mixture inclusion crystal of **1** along the channel with the crystal host. Disordered molecules are omitted for clarity.

Reference

[S1] S. Takamizawa, E. Nakata and H. Yokoyama, *Inorg. Chem. Commun.* 2003, **6**, 763.