Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Acetylene storage performance of $[Ni(4,4'\text{-bipyridine})_2(NCS)_2]_n$, a switching square lattice coordination network

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Experimental section

Synthesis of sql-1-Ni-NCS

$[Ni(bpy)_2(NCS)_2]_n$ (**sql-1-Ni-NCS**) was prepared by water slurry method. $NiSO_4 \cdot 6H_2O$ (10 mmol, 2.63 g), NaSCN (20 mmol, 1.62 g) and 4,4′-bipyridine (20 mmol, 3.12 g) were added to 50 mL water in a 100 mL bottle. The slurry was stirred continuously for 3 h at room temperature to form the precursor $\{[Ni(bpy)(NCS)_2(H_2O)_2] \cdot bpy\}_n$ which was then filtered, washed with water and air-dried (yield ~ 95%). The precursor powder was activated at 60°C in vacuo for 5 h to transform to the **sql** coordination network: **sql-1-Ni-NCS**.

Synchrotron Powder X-ray Diffraction

Synchrotron PXRD data was obtained from beamline I11 at the Diamond Light Source (λ = 0.82455(2) Å and zero point = - 0.01826(1)$^\circ$). Powder sample of **sql-1-Ni-NCS** was sealed in a Φ=0.5 mm capillary tube and then filled with C_2H_2 (195 K, 0.5 bar). Powder X-ray data (exposure time: 1 s) was collected at 1 min interval until sample stabilized using positional scanning detector (PSD).

C_2H_2 sorption experiments

C_2H_2 sorption experiments of **sql-1-Ni-NCS** were conducted on a Micromeritics 3flex instrument (195 K) and ASAP 2020 instrument (199 - 220 K). 195 K C_2H_2 experiments were maintained by a 4 L Dewar flask filled with the mixture of acetone and dry ice. 199 - 220 K C_2H_2 experiments were maintained by a LAUDA PRO RP890 Chiller.

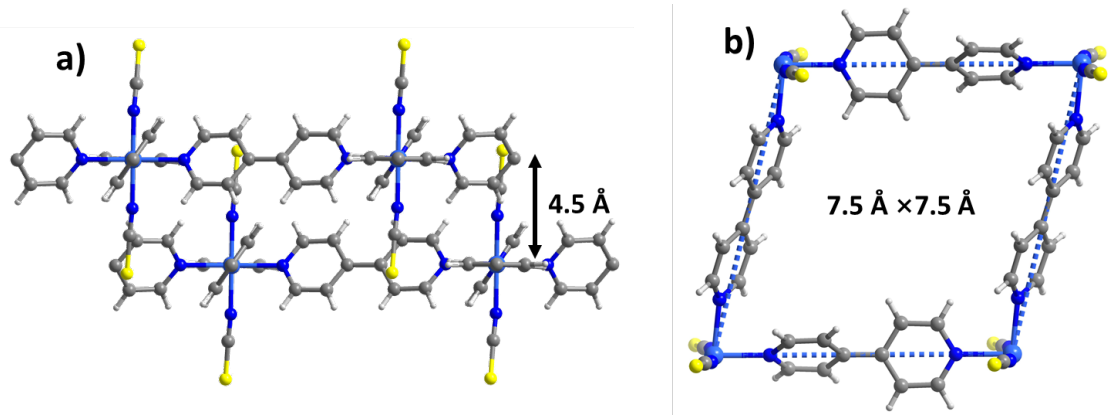

Figure S1. The crystal structure of **sql-1-Ni-NCS** reveals (a) an interlayer distance of 4.5 Å and (b) a square cavity with effective dimensions of 7.5 Å × 7.5 Å. The cavity void is filled by interdigitated NCS ligands.

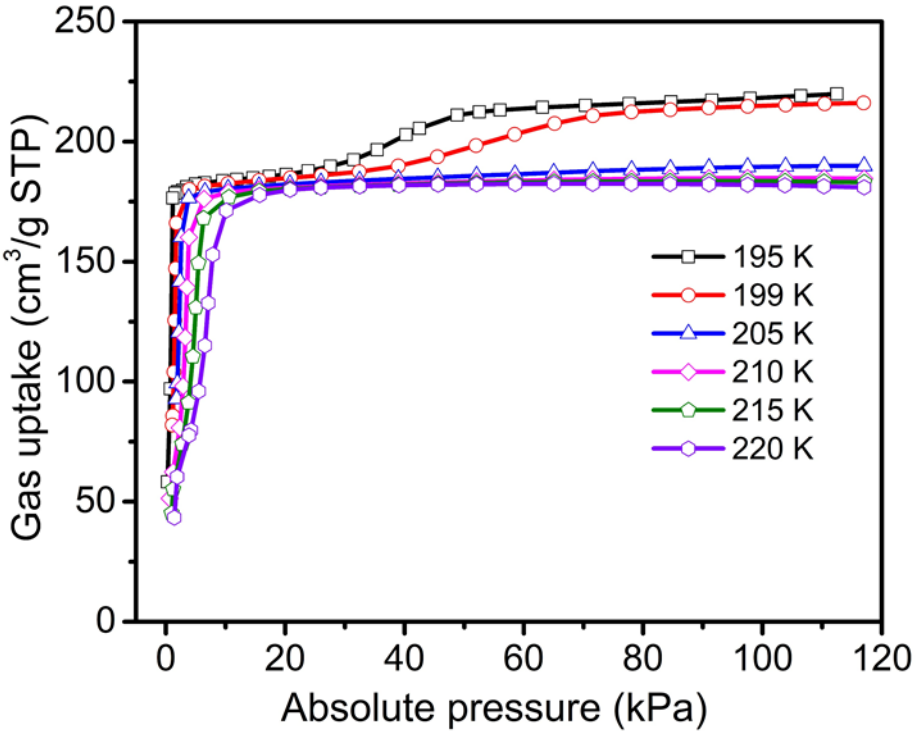

Figure S2. C_2H_2 (195 - 220 K) desorption isotherms of **sql-1-Ni-NCS**.

T/K	sql-1-Ni-NCS	
	P_{ga}/kPa	P_{gd}/kPa
195	2.9	1.3
199	4.1	1.8
205	6.8	3.0
210	10.2	4.4
215	14.9	6.3
220	21.3	9.0

sql-1-Ni-NCS
$\ln P_{ga} = -3432/T + 18.66$
$\ln P_{gd} = -3329/T + 17.33$

Equation	y = a + b*x	sql-1-Ni-NCS
Weight	No Weighting	P_{ga}
Intercept	18.66064 ± 0.03987	
Slope	-3.43184 ± 0.00825	
Residual Sum of Squares		6.71348E-5
Pearson's r	-0.99999	
R-Square(COD)	0.99998	
Adj. R-Square	0.99998	

Equation	y = a + b*x	sql-1-Ni-NCS
Weight	No Weighting	P_{gd}
Intercept	17.3294 ± 0.08513	
Slope	-3.32903 ± 0.0176	
Residual Sum of Squares		3.06054E-4
Pearson's r	-0.99994	
R-Square(COD)	0.99989	
Adj. R-Square	0.99986	

Figure S3. The linear fit parameters and results yielded from Clausius-Clapeyron equation $d\ln P/(d(1/T)) = \Delta H/R$.

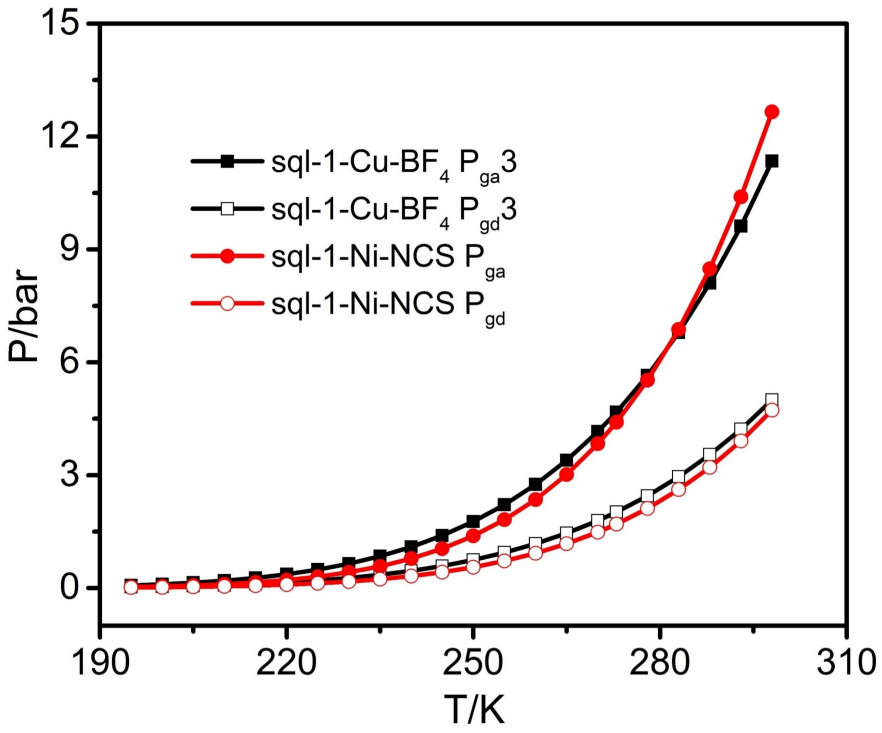

Figure S4. Comparison of the switching pressures of **sql-1-Cu-BF$_4$** and **sql-1-Ni-NCS**.

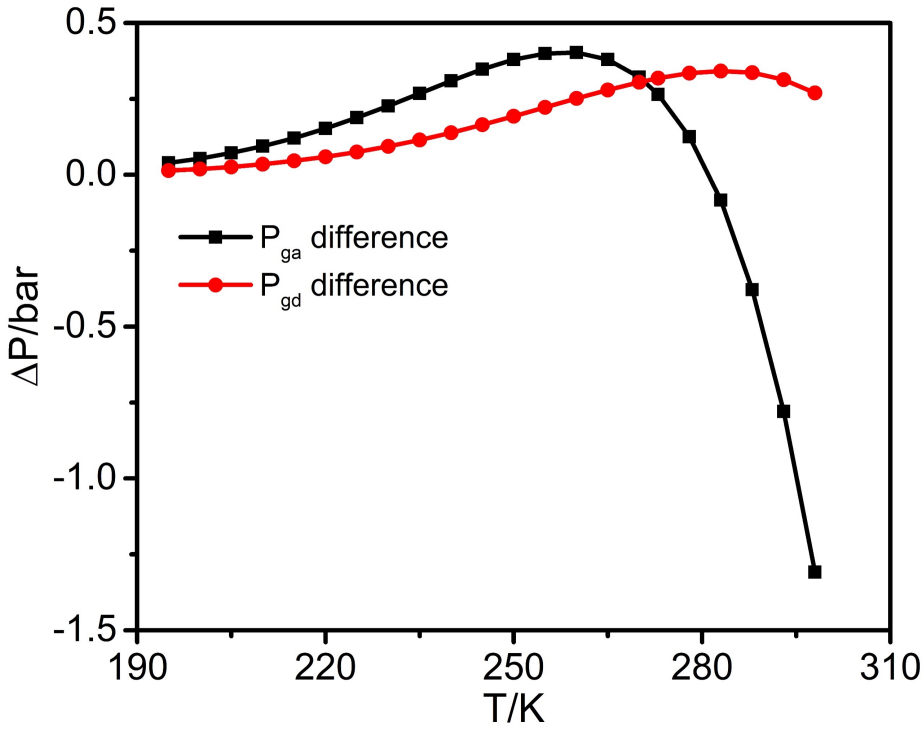

Figure S5. The switching pressure difference between **sql-1-Cu-BF$_4$** ($P_{ga}3/P_{gd}3$) and **sql-1-Ni-NCS** (P_{ga}/P_{gd}) derived from figure S4.

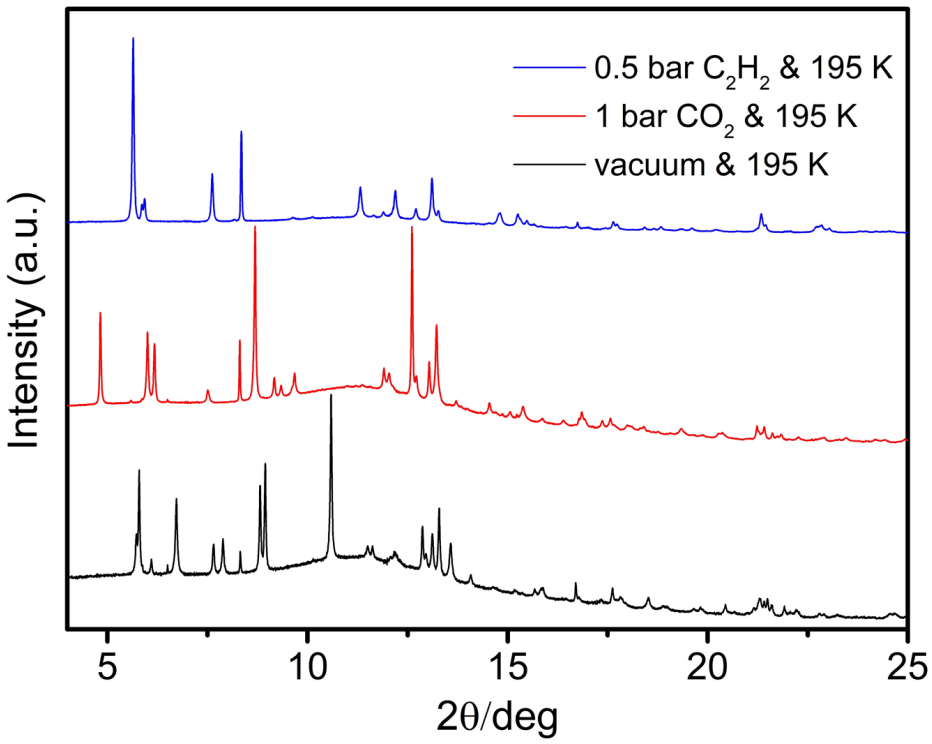

Figure S6. Comparison of synchrotron PXRD patterns of **sql-1-Ni-NCS·4C$_2$H$_2$** (blue), **sql-1-Ni-NCS·3CO$_2$** (red) and **sql-1-Ni-NCS** (black).

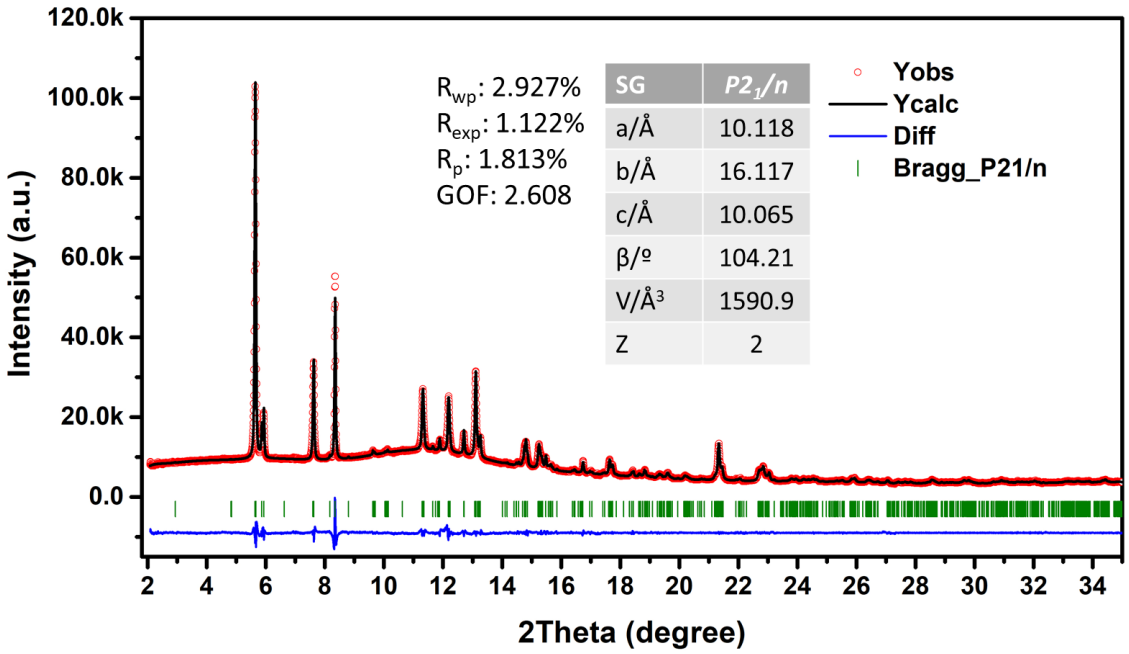

Figure S7. Synchrotron PXRD refinement results for **sql-1-Ni-NCS·4C_2H_2**.

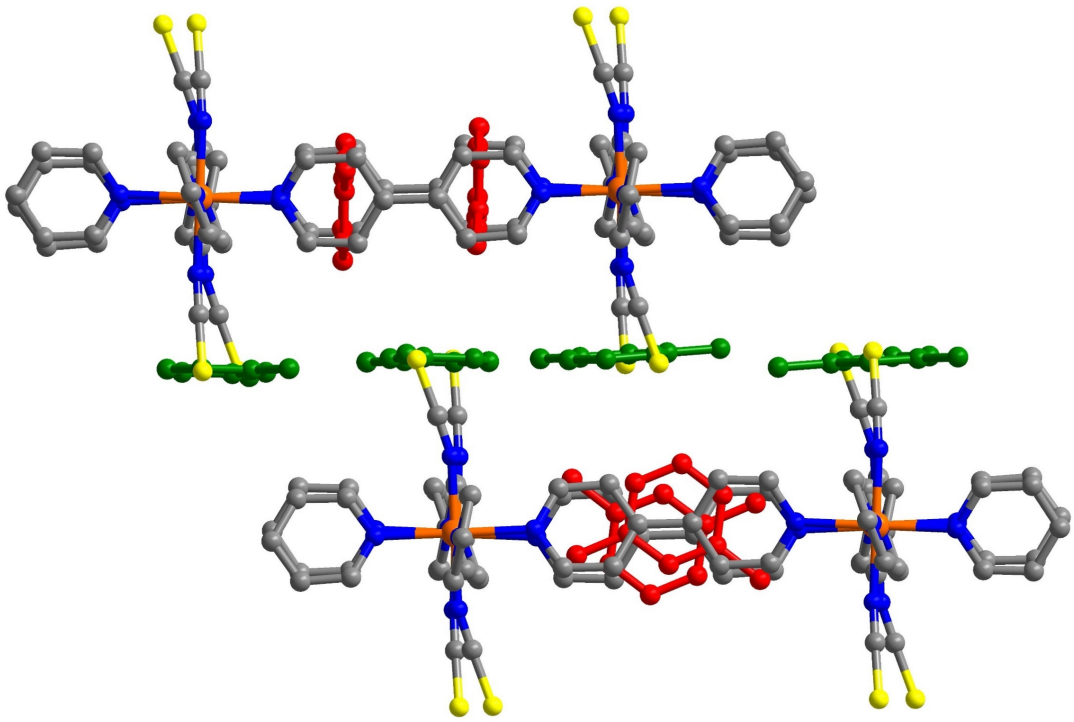

Figure S8. Crystal structure of **sql-1-Co-NCS·4MX**. Half of m-xylene molecules occupy the interlayer space (green) while the other half resides in the square cavity (red). We assume that C_2H_2 molecules in the structure of **sql-1-Ni-NCS·4C_2H_2** adopt the same packing fashion but with smaller unit-cell volume due to the relatively small kinetic diameter of C_2H_2.

Table S1. Calculated C_2H_2 switching pressures (P_{ga}/P_{gd}) and hysteresis gaps (P_{ga} - P_{gd}) for **sql-1-Ni-NCS**.

T/K	**P_{ga}/bar**	**P_{gd}/bar**	**(P_{ga} – P_{gd})/bar**
195	0.0289	0.013	0.0159
200	0.0448	0.02	0.0248
205	0.0681	0.03	0.0381
210	0.1015	0.044	0.0575
215	0.1484	0.063	0.0854
220	0.2133	0.09	0.1233
225	0.3016	0.126	0.1756
230	0.4202	0.174	0.2462
235	0.5773	0.237	0.3403
240	0.7826	0.318	0.4646
243	1.0478	0.422	0.6258
248	1.3866	0.554	0.8326
253	1.8149	0.719	1.0959
258	2.351	0.924	1.427
263	3.0159	1.177	1.8389
268	3.8332	1.485	2.3482
273	4.4079	1.7	2.7079
278	5.5262	2.117	3.4092
283	6.8731	2.616	4.2571
288	8.4838	3.208	5.2758
293	10.397	3.908	6.489
298	12.655	4.729	7.926