Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Adsorbate-dependent phase switching in the square lattice topology coordination network $[Ni(4,4'\text{-bipyridine})_2(NCS)_2]_n$

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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.[1] $NiSO_4 \cdot 6H_2O$ (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 under room temperature to form the 1D chain CP precursor $\{[Ni(bpy)(NCS)_2(H_2O)_2] \cdot bpy\}_n$ which was then filtered, washed with water and air-dried (yield ~ 95 %). The powdered precursor was activated at 60 °C in vacuo for 5 h in order to induce transformation to the guest-free **sql** coordination network **sql-1-Ni-NCS**.

Gas sorption experiments

Gas sorption experiments were conducted on a Micromeritics 3flex instrument. Around 100 mg sample of **sql-1-Ni-NCS** was used for each experiment. 77 K N_2 sorption experiments were maintained by a 4 L Dewar flask filled with liquid nitrogen. 195 K gas sorption experiments were maintained by a 4 L Dewar flask filled with the mixture of acetone and dry ice. 263 - 298 K C_3H_4 sorption experiments were maintained by a LAUDA Chiller. In our previous studies,[1–3] high pressue CO_2 sorption experiments were collected volumetrically by a Micromeritics HPVA instrument and gravimetrically by a Hiden XEMIS instrument. C_2H_2 sorption experiments (199 - 220 K) were conducted using a Micromeritics ASAP 2020 instrument. The profiles of switching gas sorption isotherms were found to be reproducible across different gas sorption instruments.

Molecular Simulations

The crystal structure of **sql-1-Ni-NCS·3CO$_2$** was determined by PXRD refinement and the locations of CO_2 molecules were calculated by density functional theory in our previous study (Fig. S6a).[1] Since CO_2 and C_3H_4 are both linear molecules with comparable kinetic diameters and exhibit the same sorption uptake (x =3), it is reasonable to assume that **sql-1-Ni-NCS·3C$_3$H$_4$** is isostructural to **sql-1-Ni-NCS·3CO$_2$**. Therefore, the structure of **sql-1-Ni-NCS·3CO$_2$** was used as the template and the CO_2 molecules were replaced by C_3H_4 in a 2×2×2 supercell (*P1* space group) using materials studio software. The coordination network was constrained by fixing atom Cartesian position and then the locations of C_3H_4 molecules were geometrically optimised using the forcite module (ultra-fine quality) implemented in materials studio (Fig. S6b).

Table S1. Switching coordination networks with at least 5 gaseous adsorbates studied.

Switching CNs	gases	Test conditions	Ref.
DUT-8(Ni)	N_2	77 K/1bar; 298 K/53 bar	4-6
	O_2	298 K/53 bar (no switching observed)	
	CH_4	298 K/36 bar (no switching observed)	
	H_2	77 K/120 bar (no switching observed)	
	Xe	165 K/1bar	
	C_4H_{10}	293 K/1 bar	
	CO_2	196 K/1 bar; 298 K/53 bar	
	C_2H_6	185 K/1bar	
	C_2H_4	169 K/1bar	
Co(bdp)	N_2	77/87 K, 1bar; 298 K, 100 bar	7-10
	H_2	50/65/77/87 K, up to 65 bar; 298 K, 100 bar	
	O_2	298 K, 1 bar (no switching observed)	
	CH_4	273/285/298/311/323 K, up to 70 bar	
	CO_2	298 K, 50 bar	
MIL-53(Fe)	CH_4	303 K, 50 bar	11-13
	C_2H_6	303 K,35 bar	
	C_3H_8	303 K, 10 bar	
	C_4H_{10}	303 K, 2 bar	
	H_2	77 K, 72 bar (no switching observed)	
	CO_2	303 K, 52 bar	
X-pcu-n-Zn	N_2	77 K, 1 bar	14,15
	CO_2	195 K, 1 bar; 273 K, 30 bar	
	CH_4	298 K, 50 bar (no switching observed)	
	C_2H_2	195/298 K, 1 bar	
	C_2H_4	195/298 K, 1 bar	
RPM3-Zn	N_2	77/298 K, 1 bar	16,17
	CO_2	278/288/298 K, 1 bar	
	Ar	87 K, 1 bar	
	H_2	298 K, 1 bar (no switching observed)	
	CH_4	298 K, 1 bar (no switching observed)	
	O_2	298 K, 1 bar (no switching observed)	
	CO	298 K, 1 bar (no switching observed)	
	C_2H_2	273/288/298 K, 1 bar	
	C_2H_4	273/288/298 K, 1 bar	
	C_2H_6	273/288/298 K, 1 bar	
	C_3H_6	298 K, 1 bar	
	C_3H_8	298 K, 1 bar	
	C_4H_{10}	298 K, 1 bar	
ELM-11	N_2	77 K, 1 bar	18-22
	O_2	77 K, 1 bar	
	Ar	77 K, 1 bar	
	CO	82 K, 1 bar	
	NO	121 K, 1 bar	
	CH_4	303 K, 60 bar	
	CO_2	195/248/258/273/298 K, 1 bar; 253 K, 20 bar; 273 K, 35 bar; 298 K, 65 bar	
	C_2H_2	189/195/200/205/210/215/220/225/230/ 273/278/283/288/293/298 K, 1 bar	
	C_2H_4	273/298 K, 1 bar	
	C_4H_{10}	273 K, 1 bar	

Table S2. Adsorbate-dependent switching easiness and sorption uptakes for selected switching CNs.

	Switching easiness	Sorption uptakes
MIL-53(Fe)	$C_4H_{10} \geq CO_2 > C_3H_8 > C_2H_6 > CH_4 >> H_2$	~ 0 -155 cc/g
X-pcu-6-Zn	$C_2H_2 > CO_2 > C_2H_4 > N_2$	~ 150 - 290 cc/g
DUT-8(Ni)	$C_4H_{10} > C_2H_6 > C_2H_4 \sim CO_2 > N_2 > CH_4 > H_2$	~ 0 - 690 cc/g
RPM3-Zn	$C_4H_{10} > C_3H_8 \sim C_3H_6 > CO_2 > C_2H_2 > C_2H_6 > C_2H_4 > Ar > N_2$	~ 25 - 135 cc/g
ELM-11	$C_4H_{10} \sim C_2H_2 > CO_2 > CH_4 > N_2$	~ 80 - 325 cc/g
Co(bdp)	$CO_2 > CH_4 > N_2 > H_2$	~ 60 - 610 cc/g

Table S3. Calculated P_{ga} values (unit: bar) of CO_2, C_2H_2, and C_3H_4 for **sql-1-Ni-NCS**.

T/K	CO_2	C_2H_2	C_3H_4
253	2.42	1.63	0.07
258	3.14	2.12	0.09
263	4.03	2.73	0.13
268	5.14	3.49	0.16
273	6.48	4.41	0.21
278	8.12	5.53	0.28
283	10.08	6.87	0.35
288	12.43	8.48	0.45
293	15.21	10.40	0.57
298	18.49	12.66	0.71

Table S4. Boiling point and vaporization enthalpy for studied gases (Source: NIST chemistry webbook).

Gases	**Boiling point/K**	**$\Delta_{vap}H$ (kJ/mol)**
N_2	77.4	5.6
CH_4	111.7	8.2
CO_2	216.6 (T_{triple})	15.3
C_2H_6	184.6	14.7
C_2H_4	169.5	13.5
C_2H_2	189.6	16.8 (200 K)
C_3H_8	231.1	19.0
C_3H_6	225.6	18.4
C_3H_4	250.0	23.0 (242 K)

Table S5. Structural parameters of previously reported **sql** CNs with chemical formula $[M(bpy)_2(NCS)_2] \cdot xG$ (**sql-1-M-NCS·*x*G**) (**M** = Fe, Co, and Ni, **G** = guest).

sql-1-M-NCS	**refcode**	**SG**	***a*/Å**	***b*/Å**	***c*/Å**	***β*/°**	**Z**	**V/Å^3**	**Ref.**
sql-1-Ni-NCS	CIZFOG	*C2/c*	12.16	11.38	16.65	100.43	4	2264.9	23
sql-1-Ni-NCS·3CO_2	TAPLUV	*C2/c*	12.60	11.37	19.56	93.40	4	2797.3	1
sql-1-Ni-NCS·4C_2H_2	-	*P2$_1$/n*	10.12	16.12	10.07	104.21	2	1590.9	3
sql-1-Co-NCS	YUVROX	*C2/c*	12.25	11.42	16.55	100.17	4	2279.6	24
	YUVROX01	*C2/c*	12.10	11.40	16.54	99.94	4	2246.6	2
sql-1-Co-NCS·3CO_2	VIBQUV	*C2/c*	12.61	11.47	19.68	92.92	4	2841.7	2
sql-1-Co-NCS·2TFT	VIBQOP	*C2/c*	23.35	11.52	13.78	108.76	4	3510.4	2
sql-1-Co-NCS·2$C_4H_{10}O$	RINPUZ	*P2/c*	11.48	11.40	13.61	107.55	2	1698.1	25
sql-1-Co-NCS·2EB	KODFIV	*C2/c*	21.85	11.47	13.44	103.14	4	3280.4	26
sql-1-Co-NCS·4OX	KODDUF	*C2/c*	20.64	11.46	22.92	116.25	4	4860.8	26
sql-1-Co-NCS·4MX	KODFAN	*P2$_1$/n*	11.39	16.10	13.33	97.91	2	2422.0	26
sql-1-Co-NCS·4PX	KODFER	*C2/c*	23.61	11.48	20.22	117.37	4	4866.4	26
sql-1-Fe-NCS	TAPLIJ	*C2/c*	12.17	11.54	16.67	100.33	4	2303.7	1
sql-1-Fe-NCS·3CO_2	TAPLOP	*C2/c*	12.58	11.54	19.81	92.57	4	2871.6	1
sql-1-Fe-NCS·2S_8	ETOFAW	*C2/c*	21.25	11.59	16.46	105.75	4	3902.0	27
sql-1-Fe-NCS·2C_2HCl_3	QAGVUR	*C2/c*	22.51	11.55	12.36	103.30	4	3128.3	28
sql-1-Fe-NCS·2MB	QAGWAY	*C2/c*	21.33	11.58	12.99	99.35	4	3167.5	28
sql-1-Fe-NCS·2NB	QAGWEC	*C2/c*	22.47	11.61	13.21	103.08	4	3354.2	28
sql-1-Fe-NCS·2$C_4H_{10}O$	QAGWIG	*P2/c*	11.52	11.48	13.10	106.60	2	1660.4	28
sql-1-Fe-NCS·3CS_2	QAGXED	*P2/c*	11.53	11.54	12.75	110.83	2	1585.5	28
sql-1-Fe-NCS·3MeOH	QAGWUS	*C2/c*	16.05	16.61	12.60	120.58	4	2891.8	28
sql-1-Fe-NCS·2NM·MeOH	QAGXAZ	*C2/c*	16.42	16.38	12.55	120.21	4	2916.2	28
sql-1-Fe-NCS·4C_3H_6O	QAGWOM	*P2/c*	11.55	11.54	15.45	114.37	2	1875.7	28
sql-1-Fe-NCS·4$CHCl_3$	QAQTOT	*C2/c*	22.68	22.62	17.29	117.76	8	7849.7	29

Note: SG = space group; TFT = trifluorotoluene; EB = ethylbenzene; OX = *o*-xylene; MX = *m*-xylene; PX = *p*-xylene; MB = methylbenzene; NB = nitrobenzene; NM = nitromethane.

Table S6. Category of **sql-1-M-NCS·*x*G** classified by unit cell volume increase as indicated in Fig. S5.

Category	Volume increase/%	Guest molecules per formular unit
A	23.5 - 28.8	3CO_2; 3MeOH; 2NM+MeOH
B	38.1 - 40.5	2C_2HCl_3; 2MB; 3CS_2; 4C_2H_2
C	44.8 - 55.0	2EB; 2$C_4H_{10}O$; 2NB; 2TFT
D	65.6 - 73.3	4C_3H_6O; 2S_8; 4$CHCl_3$
E	113.9 - 114.9	4OX; 4MX; 4PX

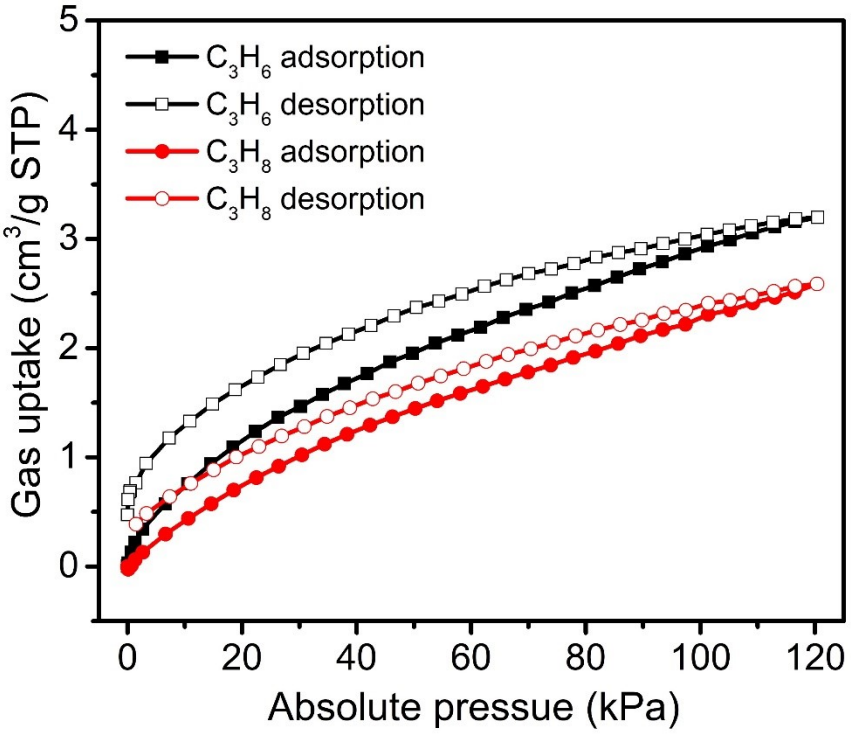

Figure S1. 273 K C_3H_6 and C_3H_8 sorption isotherms of **sql-1-Ni-NCS**.

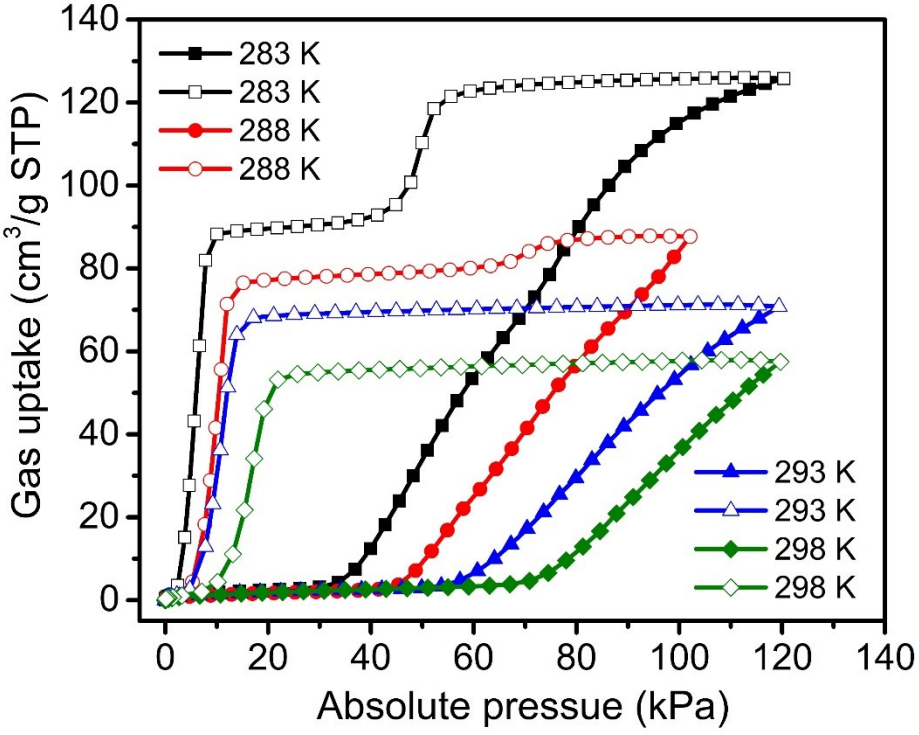

Figure S2. C_3H_4 (283 - 298 K) sorption isotherms of **sql-1-Ni-NCS**.

T/K	263	268	273	278	283	288
P_{ga}/kPa	12.5	16.5	21.5	28.0	35.5	45.0

Equation y = a + b*x
Weight No Weighting
Intercept 17.29343 ± 0.05712
Slope -3.88334 ± 0.01571
Residual Sum of Squares 7.53188E-5
Pearson's r -0.99997
R-Square(COD) 0.99993
Adj. R-Square 0.99992

$Ln(P_{ga}/kPa) = -3883/T+17.29$; $\Delta H = -32.3$ kJ/mol

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

The lower the switching pressure, the easier the switching can occur.

C_3H_4 (298 K, 0.71 bar) > C_2H_2 (298 K, 12.66 bar) > CO_2 (298 K, 18.49 bar)

CO_2 (195 K, 0.1 bar) > C_2H_4 (195 K, 0.86 bar) > C_2H_6 (195 K, 0.91 bar)

> CH_4 (195 K, no switching before 1 bar) ≥ N_2 (77 K, no switching before 1 bar)

Figure S4. Analysis of the switching easiness based on the switching pressure under same temperatures.

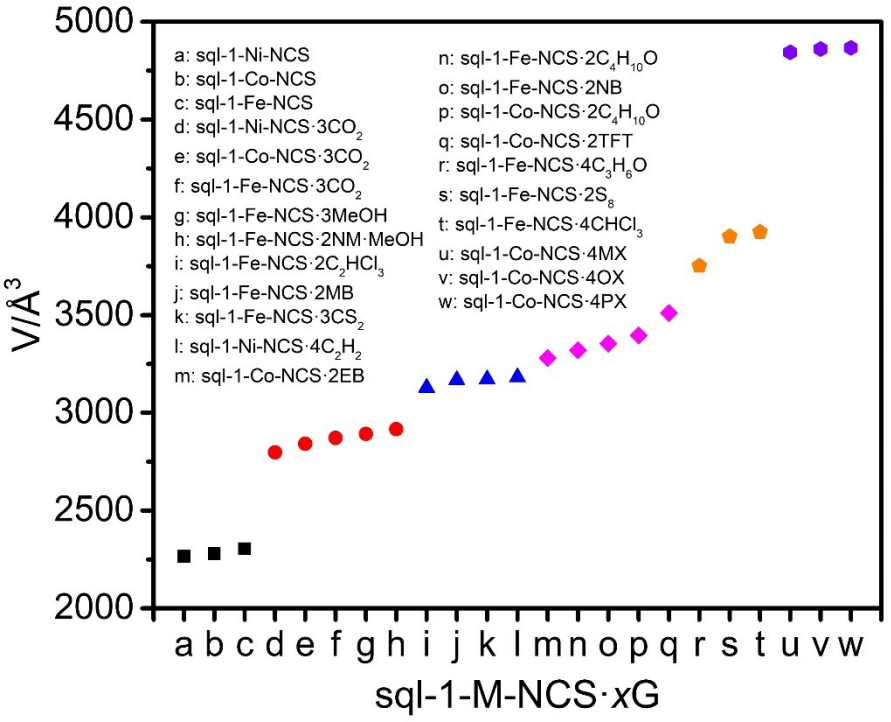

Figure S5. Unit-cell volume (Z value normalized to 4) of **sql-1-M-NCS·*x*G** as listed in Table S5.

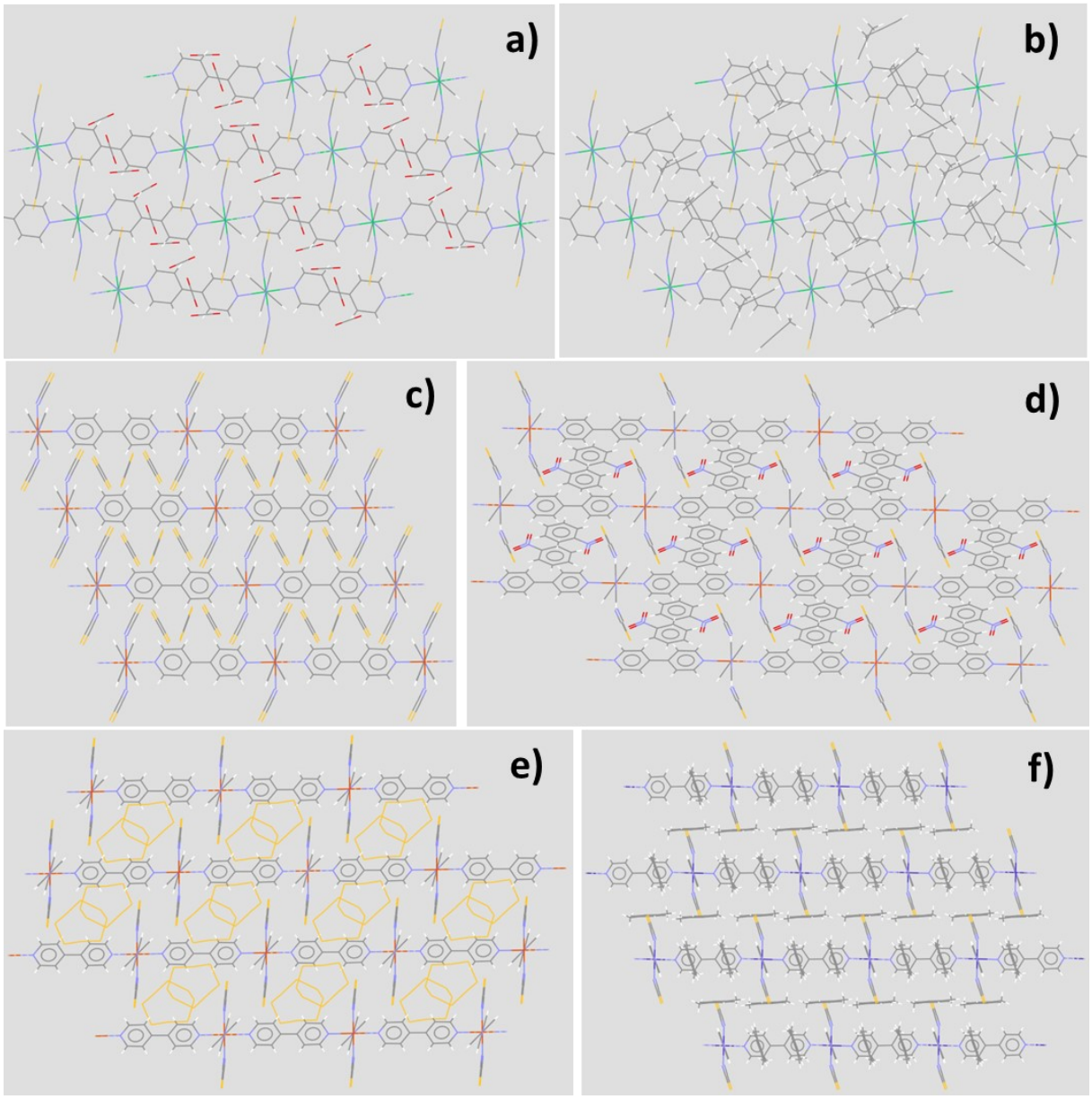

Figure S6. Layer packing modes (viewed along ***b*** axis) of **sql-1-Ni-NCS·*x*G** from each category as listed in Table S6: a) **sql-1-Ni-NCS·3CO$_2$,** b) **sql-1-Ni-NCS·3C$_3$H$_4$** (this work), c) **sql-1-Fe-NCS·3CS$_2$**, d) **sql-1-Fe-NCS·2NB**, e) **sql-1-Fe-NCS·2S$_8$**, and f) **sql-1-Co-NCS·4PX**.

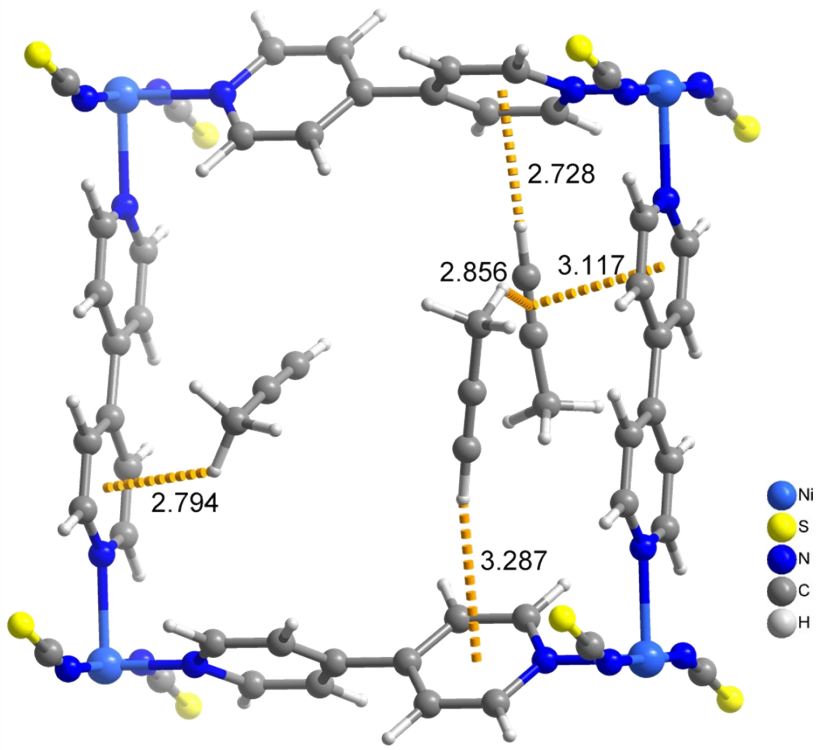

Figure S7. Host-guest interactions (C-H···π and π···π, unit: Å) in **sql-1-Ni-NCS·3C$_3$H$_4$** as determined by molecular simulations.

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