

Supporting Information

Aromatic Guest–Induced Layer Expansion and Phase Switching in a 2D Square Lattice Coordination Network

*Shi-Qiang Wang,^{*a} Shaza Darwish,^b Shan Xu,^a Rong Wang,^{*a}, and Michael J. Zaworotko^{*b}*

*^aSingapore Membrane Technology Centre, Nanyang Environment and Water Research Institute, Nanyang Technological University, 1
Cleantech Loop, 637141, Singapore.*

^bBernal Institute and Department of Chemical Sciences, University of Limerick, Limerick V94 T9PX, Republic of Ireland.

**E-mail: shiqiang.wang@ntu.edu.sg; rwang@ntu.edu.sg; xtal@ul.ie*

Table S1. Crystallographic data of **sql-1-M-NCS·xG**.

	sql-1-Fe-NCS·2MB	sql-1-Co-NCS·2NB	sql-1-Co-NCS·3TMB
Formula	[Fe(C ₁₀ H ₈ N ₂) ₂ (NCS) ₂] ₂ ·2(C ₇ H ₈)	[Co(C ₁₀ H ₈ N ₂) ₂ (NCS) ₂] ₂ ·2(C ₆ H ₅ NO ₂)	[Co(C ₁₀ H ₈ N ₂) ₂ (NCS) ₂] ₃ ·3(C ₉ H ₁₂)
Formula weight	668.64	733.68	848.01
Temperature/K	100	273	100
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	<i>C2/c</i>	<i>C2/c</i>	<i>P-1</i>
<i>a</i> /Å	21.3414	22.496	11.4865
<i>b</i> /Å	11.5792	11.500	11.5252
<i>c</i> /Å	12.9982	13.512	17.5412
<i>α</i> /°	90	90	77.040
<i>β</i> /°	99.3030	105.196	86.422
<i>γ</i> /°	90	90	88.358
Volume/Å ³	3169.8	3373.4	2258.4
<i>Z</i>	4	4	2
CCDC No.	2543884	2543885	2543886

MB = methylbenzene, NB = nitrobenzene, TMB = 1,3,5-trimethylbenzene

Table S2. Physical properties of studied aromatic molecules.

chemicals	formula	M (g/mol)	bp (°C)	vapor pressure at 25 °C (kPa)
MB	C ₇ H ₈	92.14	110.6	3.79
EB	C ₈ H ₁₀	106.17	136	1.33
NB	C ₆ H ₅ NO ₂	123.11	210.9	0.03
TFT	C ₇ H ₅ F ₃	146.11	103.5	1.5
TMB	C ₉ H ₁₂	120.19	164.7	0.33
OX	C ₈ H ₁₀	106.17	144.4	0.88
MX	C ₈ H ₁₀	106.17	139	1.12
PX	C ₈ H ₁₀	106.17	138	1.18

Table S3. Aromatic guest-induced layer expansion of **sql-1-M-A**.

Compounds	Interlayer distance (Å)	Reported Year	Refcode
sql-1-Cd-NO ₃ ·2DBB	6.35	1994	YECFAN
sql-1-Cd-NO ₃ ·2 <i>o</i> -NA	6.11	1999	DIDLIL
sql-1-Co-NO ₃ ·3Nap	7.81	1999	QOZLAS
sql-1-Ni-NO ₃ ·3Nap	7.76	1999	QOZLEW
sql-1-Ni-NO ₃ ·2pyrene	7.91	1999	GOSSEM
sql-1-Ni-NO ₃ ·2DCB	6.24	2000	METMON
sql-1-Ni-NO ₃ ·2Bz	5.89	2000	METMUT
sql-1-Ni-NO ₃ ·2NB	6.04	2000	METNAA
sql-1-Co-NO ₃ ·2DCB	6.19	2000	METNEE

sql-1-Co-NO ₃ ·2Bz	5.83	2000	METNII
sql-1-Co-NO ₃ ·2NB	6.00	2000	METNOO
sql-1-Co-NO ₃ ·2MB	6.01	2000	METNUU
sql-1-Co-NO ₃ ·3An	7.72	2000	METPAC
sql-1-Ni-NO ₃ ·2CB	6.05	2000	METPEG
sql-1-Co-NO ₃ ·2CB	6.02	2000	METPIK
sql-1-Cu-NO ₃ ·3PABA	8.84	2000	LONTAJ
sql-1-Co-NO ₃ ·2 <i>p</i> -NA	6.24	2001	ODAGOP
sql-1-Ni-NO ₃ ·2 <i>p</i> -NA	6.32	2001	ODAGUV
sql-1-Zn-NO ₃ ·2 <i>p</i> -NA	6.26	2001	ODAHAC
sql-1-Zn-NO ₃ ·pyrene·2DCB	8.15	2007	XIJQUD
sql-1-Cd-NCS·PTDS	9.06	2009	MUFTIR
sql-1-Fe-NCS·2MB	5.92	2010	QAGWAY
sql-1-Fe-NCS·2NB	6.19	2010	QAGWEC
sql-1-Co-NCS·2TFT	6.63	2018	VIBQOP
sql-1-Co-NCS·4OX	9.26	2019	KODDUF
sql-1-Co-NCS·4MX	9.21	2019	KODFAN
sql-1-Co-NCS·4PX	9.15	2019	KODFER
sql-1-Co-NCS·2EB	6.25	2019	KODFIV
sql-1-Co-NCS·4OX	9.58	2023	VEQNIS02
sql-1-Cu-CF ₃ CO ₂ ·2TFT	7.70	2025	ZADTAE
sql-1-Cu-CF ₃ CO ₂ ·2OX	7.66	2025	ZADTEI
sql-1-Cu-CF ₃ CO ₂ ·2MX	7.80	2025	ZADTIM
sql-1-Cu-CF ₃ CO ₂ ·1PX	6.83	2025	ZADTOS

DBB = *o*-dibromobenzene; *o*-NA = *o*-nitroaniline; Nap = naphthalene; DCB = *o*-dichlorobenzene; Bz = benzene; NB = nitrobenzene; MB = methylbenzene (toluene); An = anisole; CB = chlorobenzene; PAPB = 4-aminobenzic acid; *p*-NA = *p*-nitroaniline; PTDS = *p*-toyldisulfide; TFT = α,α,α -trifluorotoluene; OX = *o*-xylene; MX = *m*-xylene; PX = *p*-xylene; EB = ethylbenzene

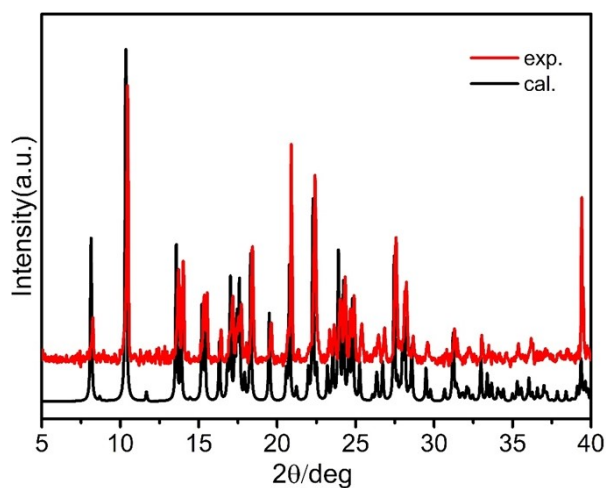


Figure S1. Calculated and experimental PXRD patterns of **sql-1-Co-NCS·2NB**.

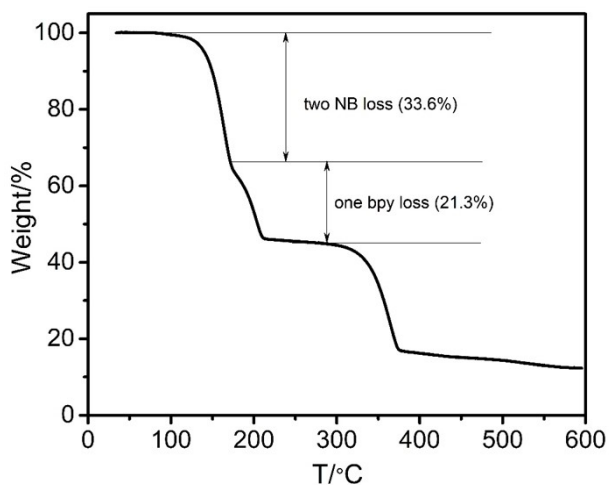


Figure S2. TGA curve of **sql-1-Co-NCS·2NB**.

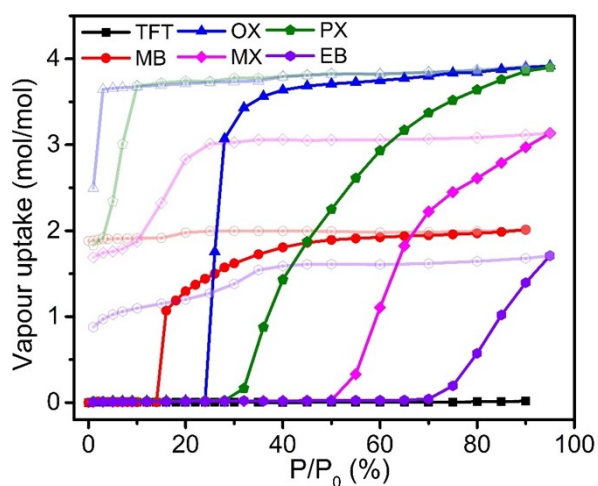


Figure S3. Vapor adsorption isotherms (298 K) of **sql-1-Co-NCS**. Vapor uptake is expressed in mol/mol. Adsorption: solid symbols; desorption: open symbols.