Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Phase switching and shape-memory effect in a molecular material: revisiting the Werner complex $[Ni(4\text{-}MePy)_4(NCS)_2]$

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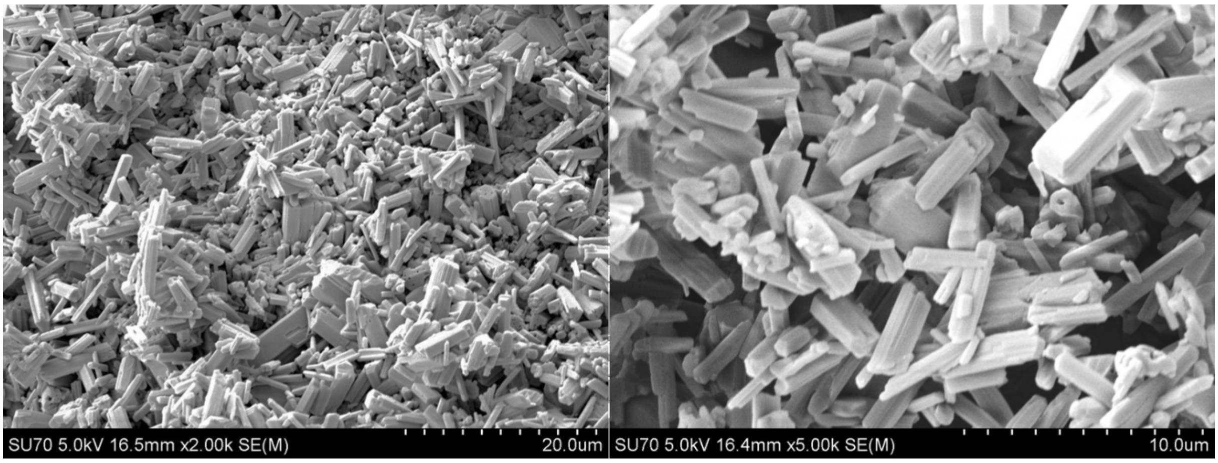

Figure S1. SEM images of the as-made powder sample of [Ni(4-MePy)$_4$(NCS)$_2$]-**α**.

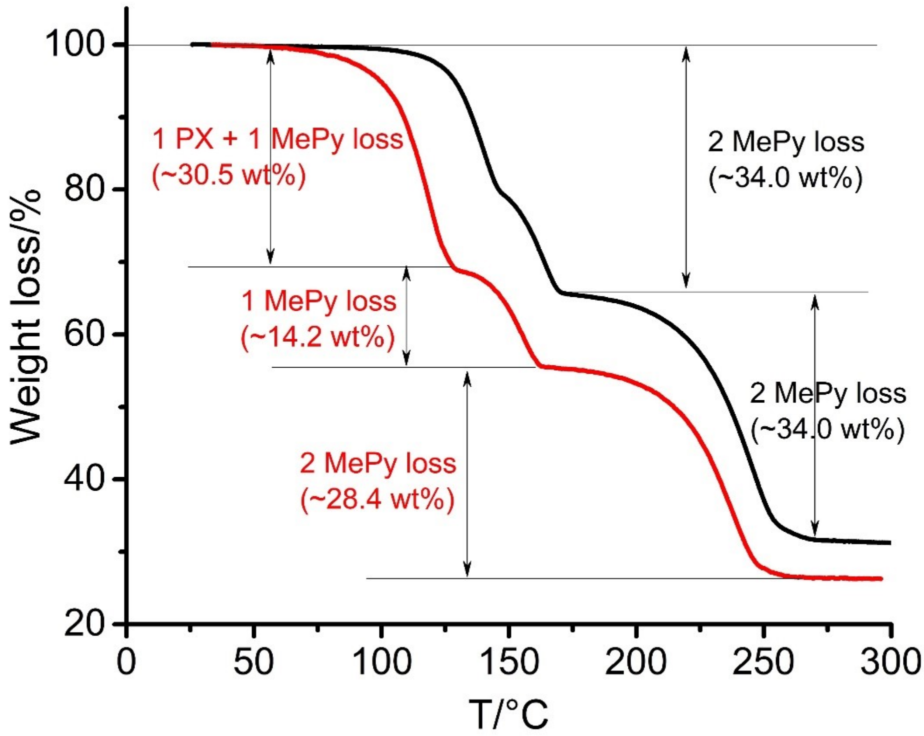

Figure S2. TGA curves of the closed **α** (black line) and PX-loaded **β** (red line) phases of [Ni(4-MePy)$_4$(NCS)$_2$].

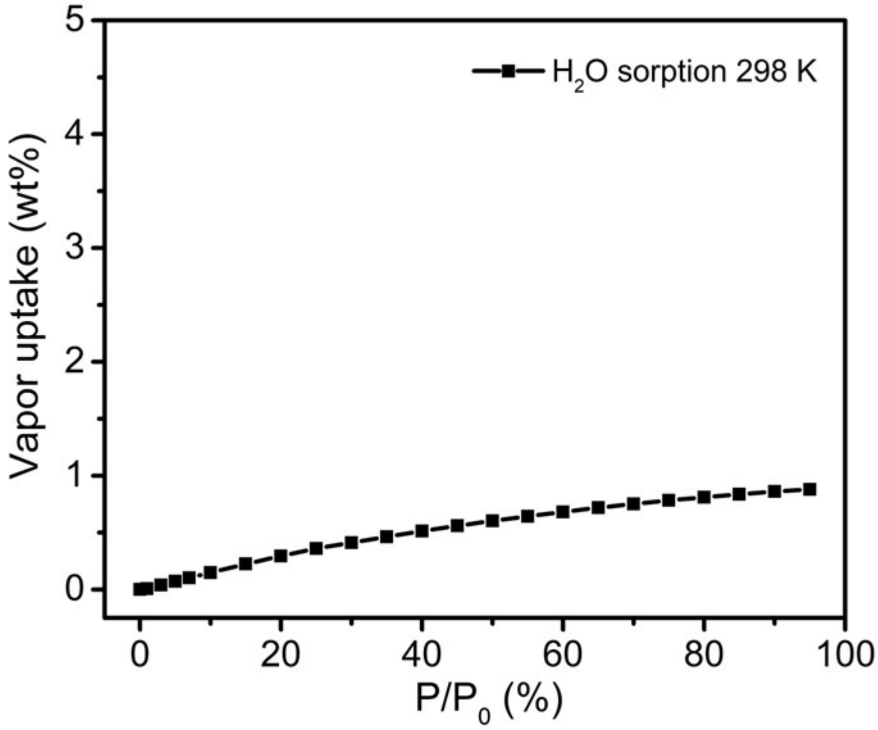

Figure S3. Water vapor sorption isotherm (298 K) of the as-made [Ni(4-MePy)$_4$(NCS)$_2$]-**α**.

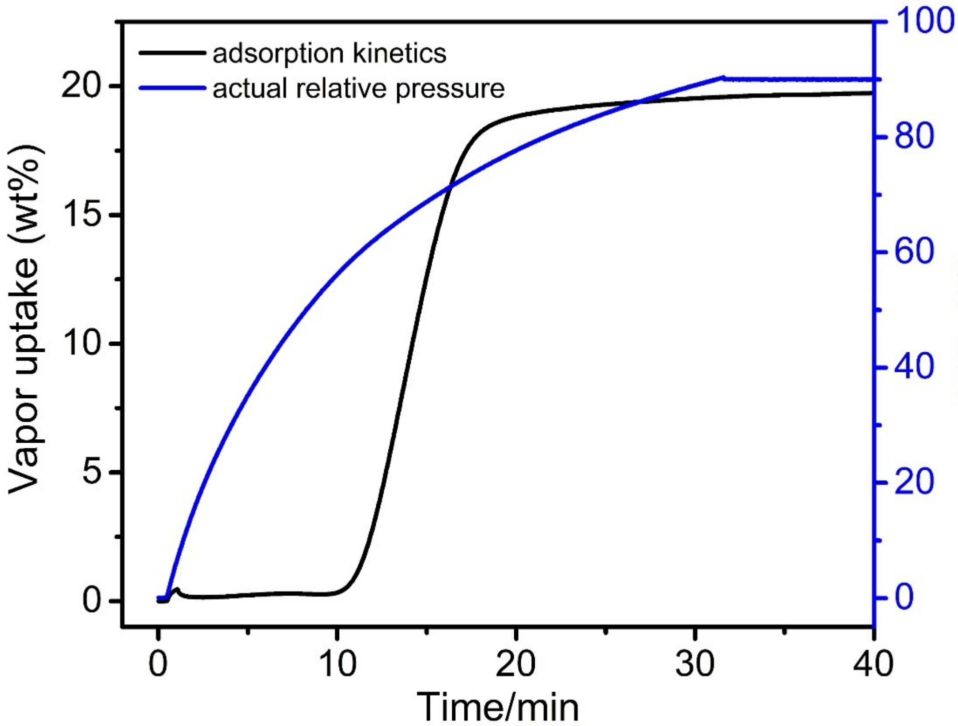

Figure S4. PX sorption kinetics test (298 K) of the single-crystal form of [Ni(4-MePy)$_4$(NCS)$_2$]-**α**.

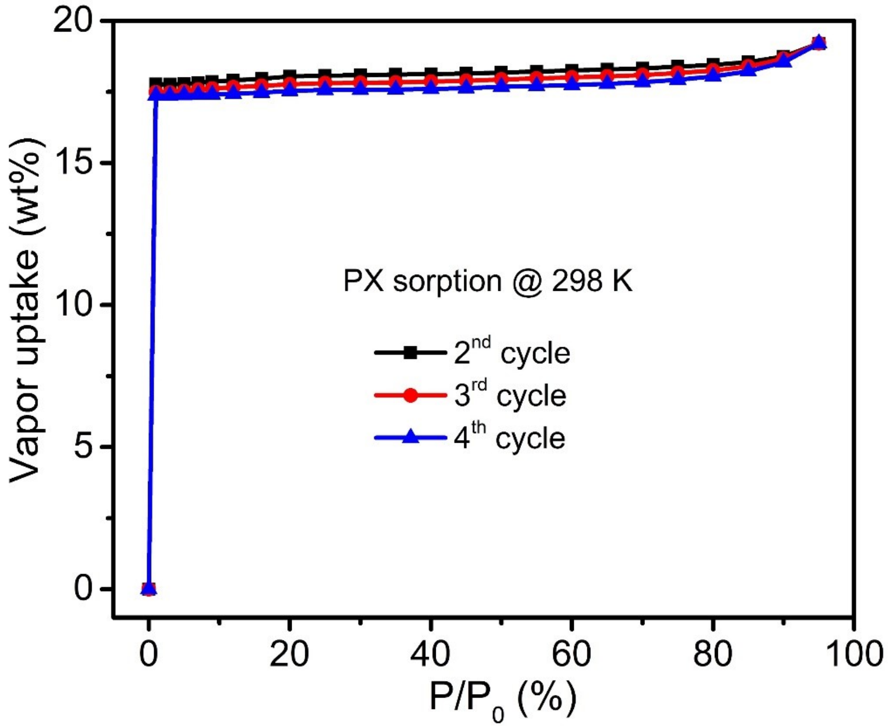

Figure S5. The recyclability test of the open-empty **β′** phase of [Ni(4-MePy)$_4$(NCS)$_2$].

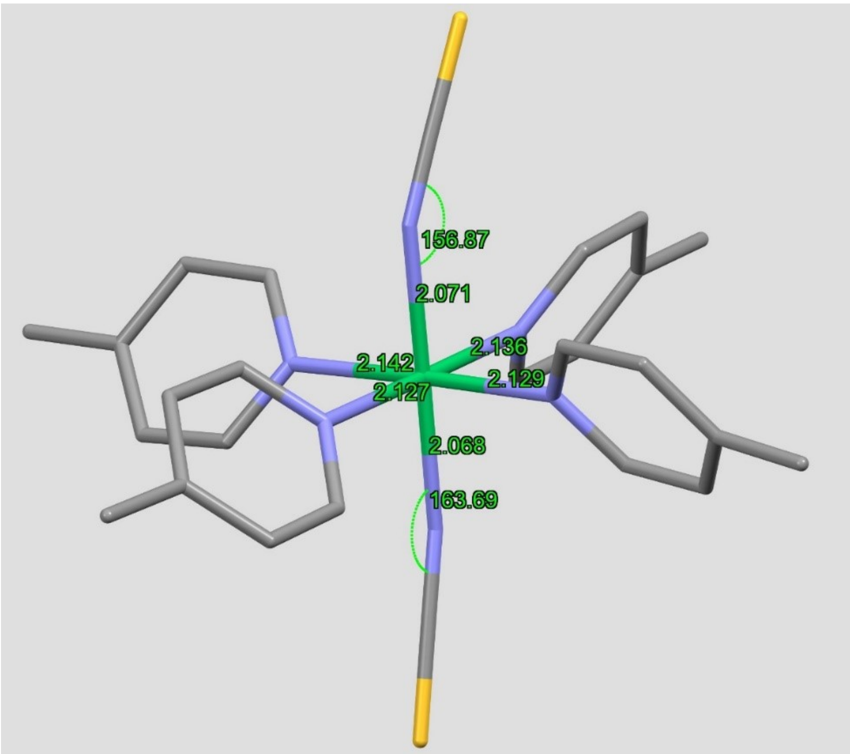

Figure S6. Crystal structural information of [Ni(4-MePy)$_4$(NCS)$_2$]-**α** (refcode: ICMPNI03).

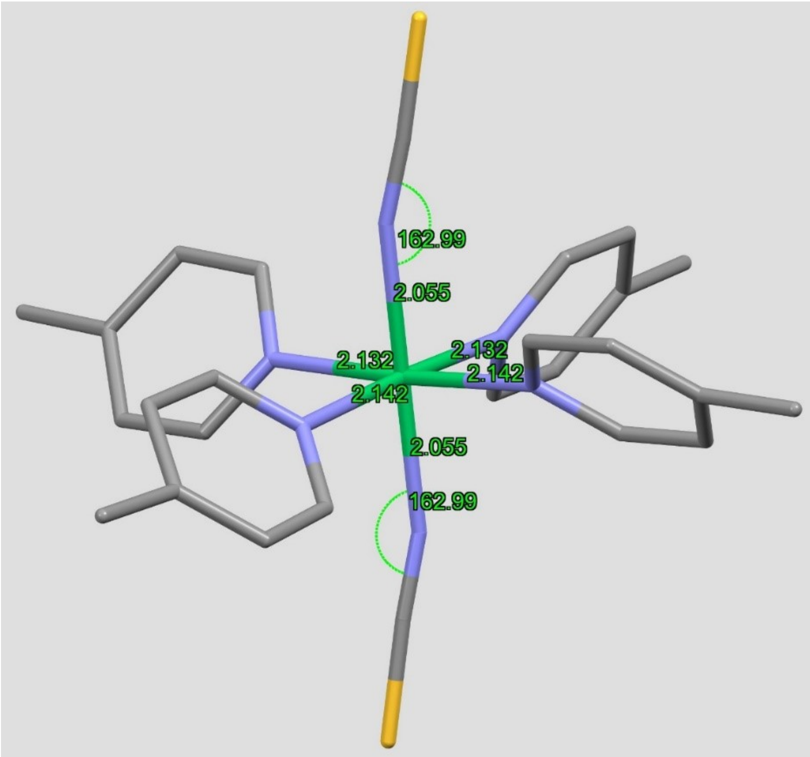

Figure S7. Crystal structural information of [Ni(4-MePy)$_4$(NCS)$_2$]-PX (refcode: BAPZAT).

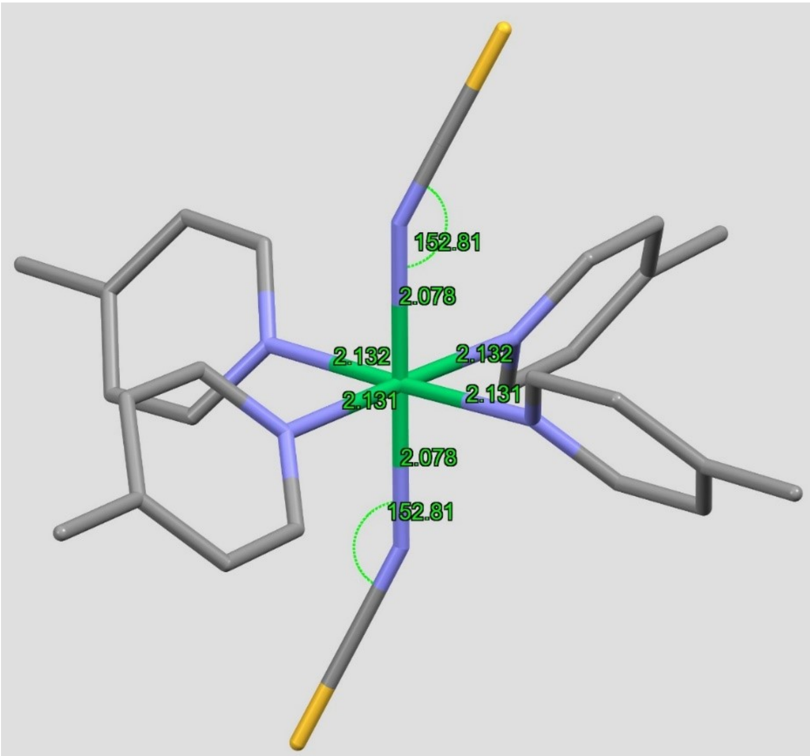

Figure S8. Crystal structural information of [Ni(4-MePy)$_4$(NCS)$_2$]-**β′** (refcode: ICMPNI04).

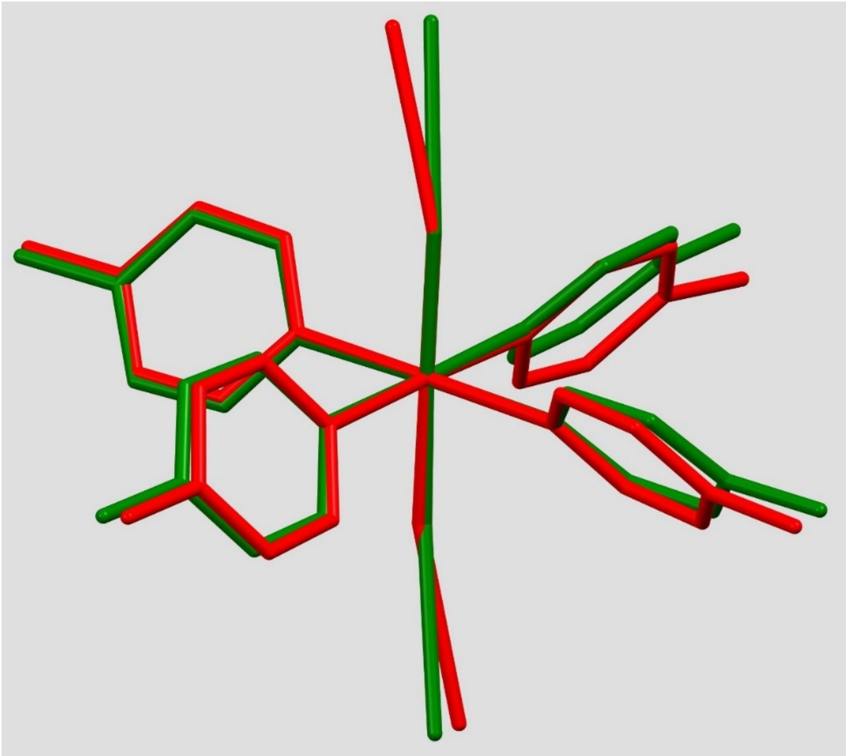

Figure S9. Structural overlay of the closed (red) and open-empty (green) phases of [Ni(4-MePy)$_4$(NCS)$_2$].

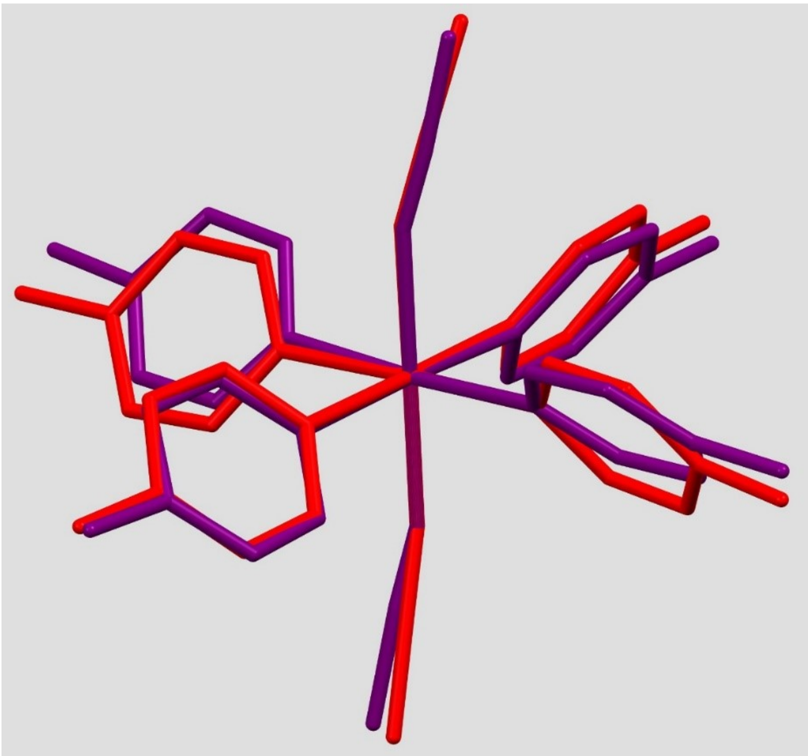

Figure S10. Structural overlay of the closed (red) and PX-loaded (purple) phases of [Ni(4-MePy)$_4$(NCS)$_2$].

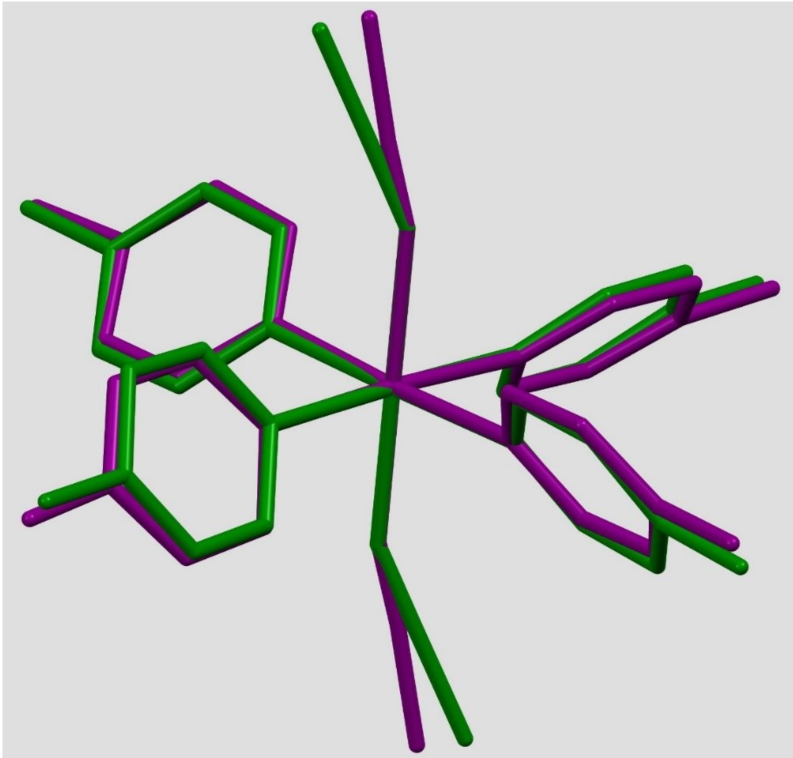

Figure S11. Structural overlay of the open-empty (green) and PX-loaded (purple) phases of [Ni(4-MePy)$_4$(NCS)$_2$].

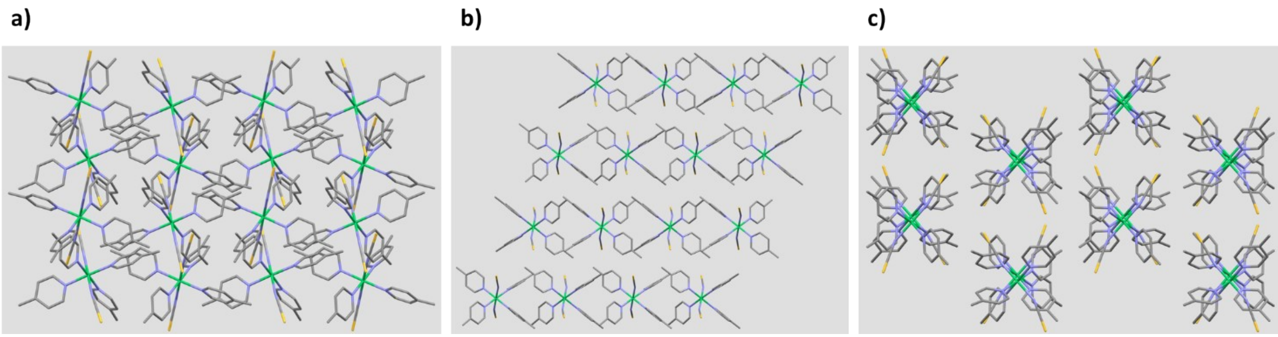

Figure S12. Packing mode of [Ni(4-MePy)$_4$(NCS)$_2$]-***α*** along a) ***a***, b) ***b***, and c) ***c*** axis (refcode: ICMPNI03).

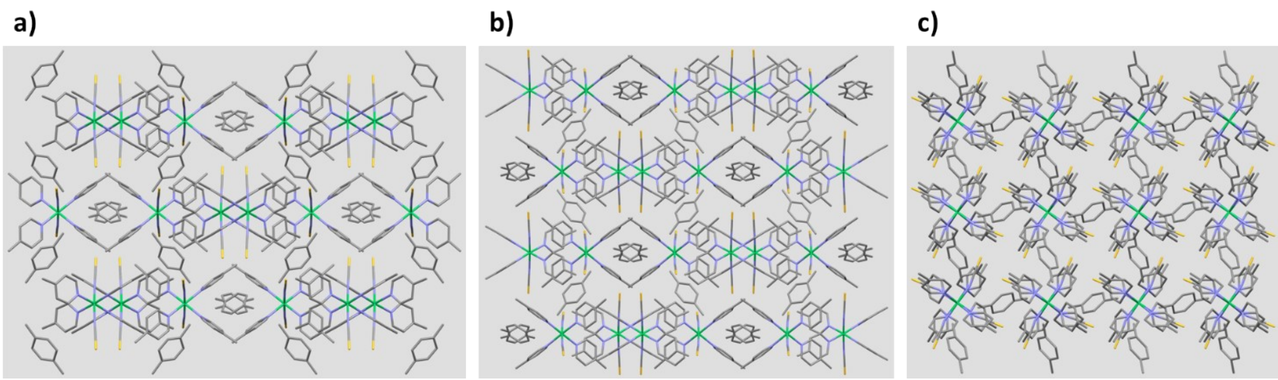

Figure S13. Packing mode of [Ni(4-MePy)$_4$(NCS)$_2$]-PX along a) ***a***, b) ***b***, and c) ***c*** axis (refcode: BAPZAT).

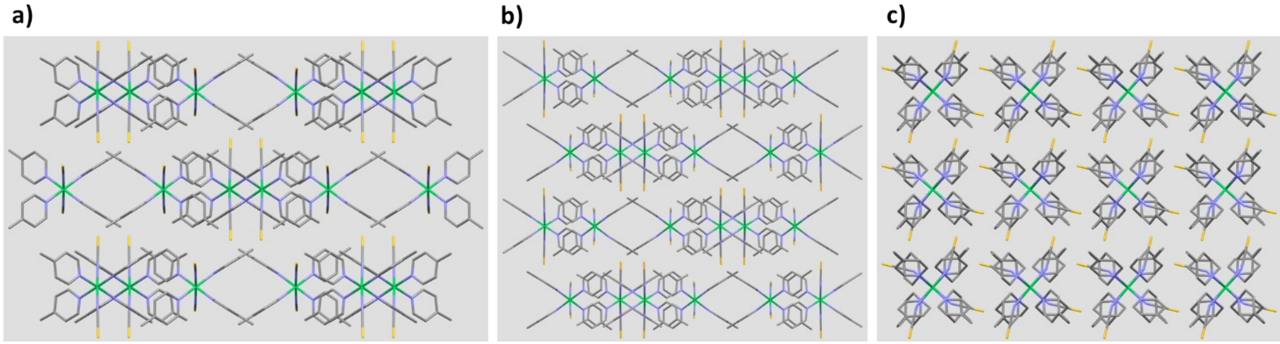

Figure S14. Packing mode of [Ni(4-MePy)$_4$(NCS)$_2$]-**β′** along a) ***a***, b) ***b***, and c) ***c*** axis (refcode: ICMPNI04).

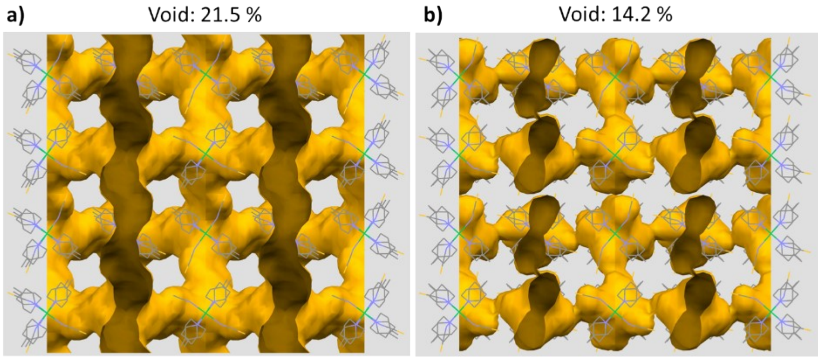

Figure S15. Crystal structural void analysis of a) [Ni(4-MePy)$_4$(NCS)$_2$]-PX (PX molecule is excluded) and b) [Ni(4-MePy)$_4$(NCS)$_2$]-**β′**. The probe radius is 1.2 Å.

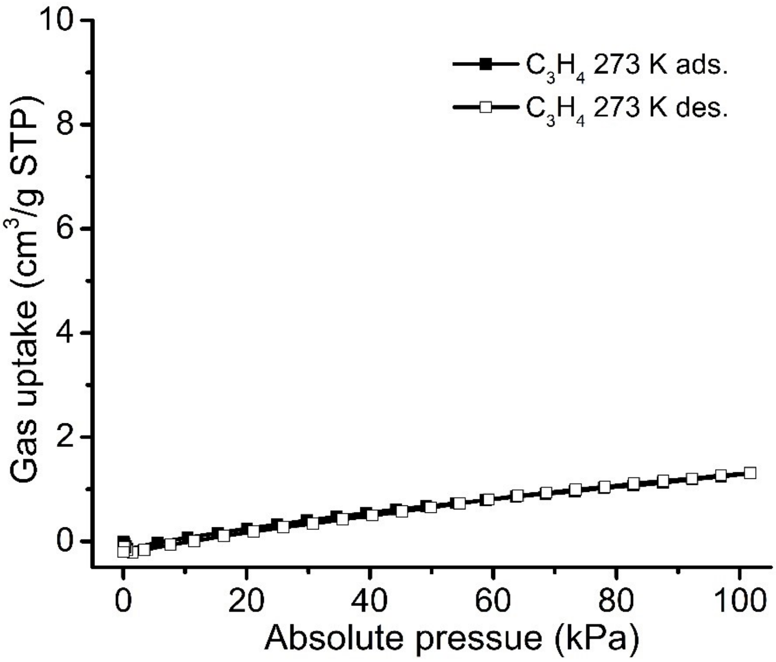

Figure S16. 273 K C_3H_4 sorption isotherms for [Ni(4-MePy)$_4$(NCS)$_2$]-**α**.

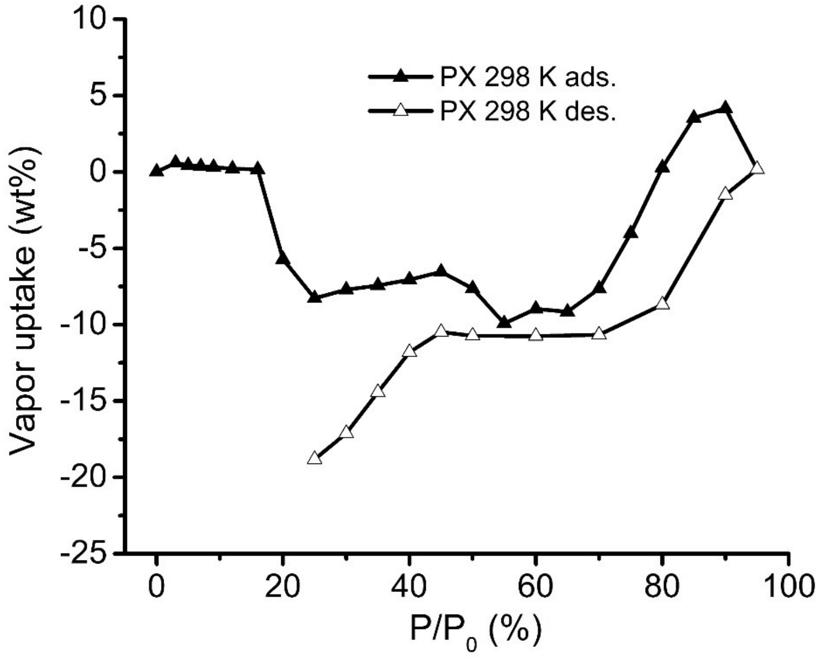

Figure S17. PX vapor sorption isotherms (298 K) of the regenerated $[Ni(4\text{-}MePy)_4(NCS)_2]$-**α**.

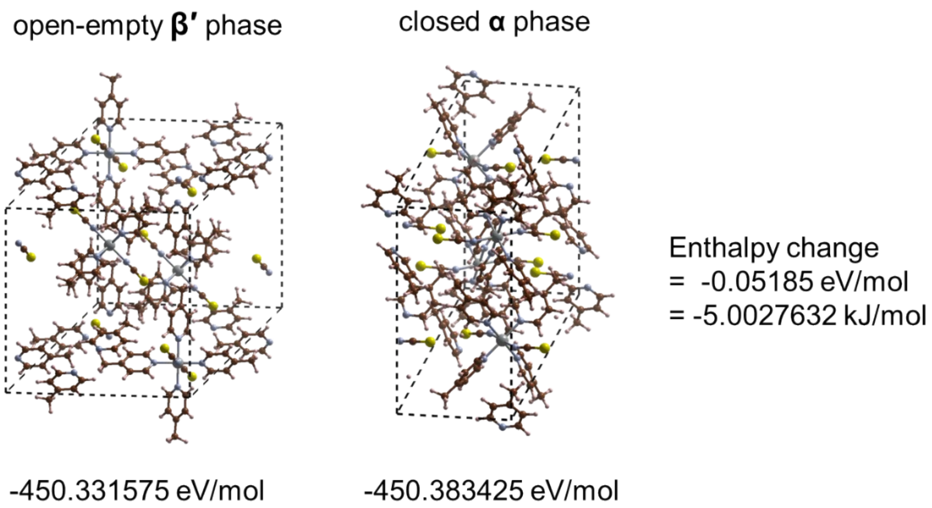

Fig. S18. Enthalpy change between the **α** and **β′** phases calculated by the density functional theory.

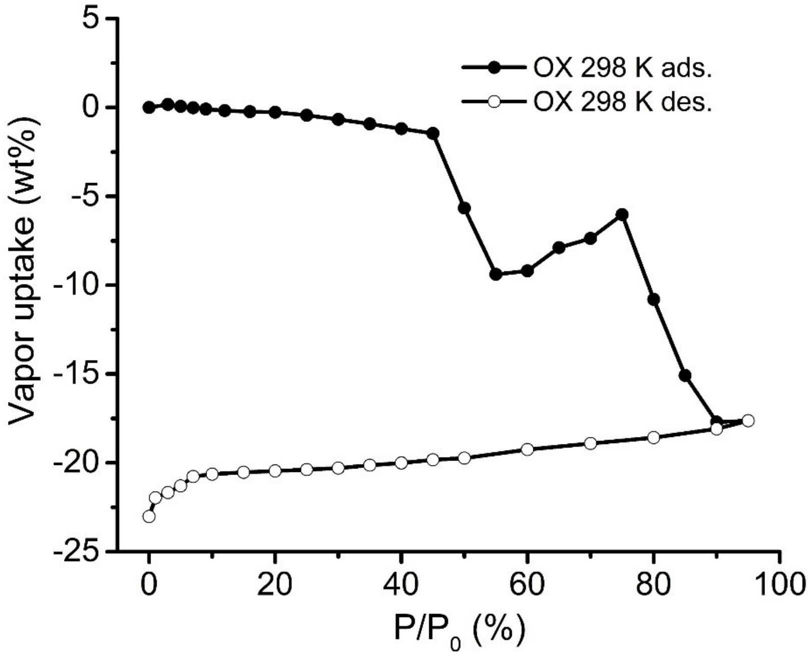

Figure S19. OX vapor sorption isotherms (298 K) of [Ni(4-MePy)$_4$(NCS)$_2$]-**α**.

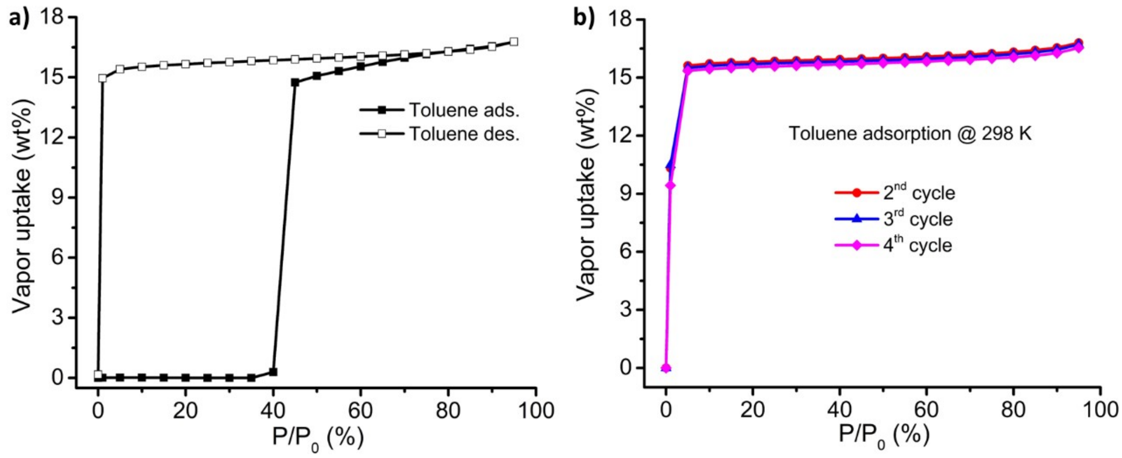

Figure S20. Toluene sorption (298 K) on [Ni(4-MePy)$_4$(NCS)$_2$]-**α**: a) first cycle, and b) the subsequent 2-4 cycles.

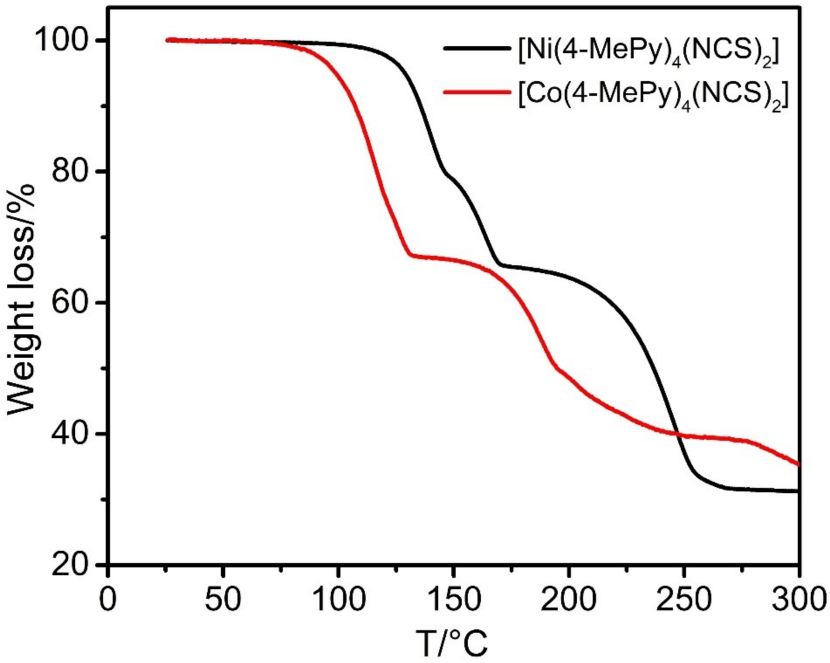

Figure S21. Comparison of the thermal stability between $[Co(4\text{-}MePy)_4(NCS)_2]$ and $[Ni(4\text{-}MePy)_4(NCS)_2]$.

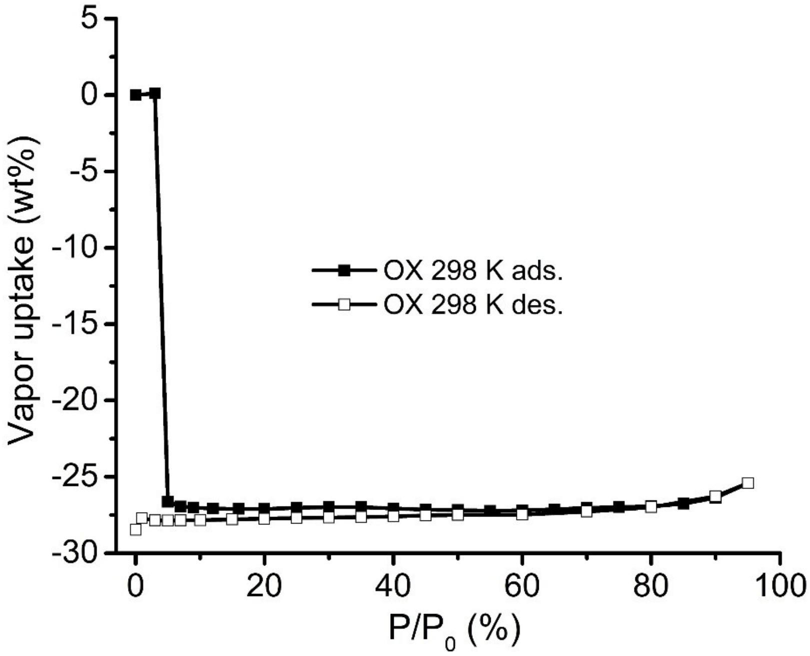

Figure S22. OX vapor sorption isotherms (298 K) of $[Co(4\text{-}MePy)_4(NCS)_2]$-**α**.

Table S1. Summary of different guest-loaded $[Ni(4\text{-}MePy)_4(NCS)_2]$-**β** phases with space group *I4₁/a*.

formula	a	c	V	refcode	Year	Ref.
$[Ni(4\text{-}MePy)_4(NCS)_2]\cdot 0.53PX$	16.79	22.40	6315.4	ZZZUXE	1963	1
$[Ni(4\text{-}MePy)_4(NCS)_2]\cdot 0.94C_6H_6$	16.67	22.74	6319.2	ZZZUXK		
$[Ni(4\text{-}MePy)_4(NCS)_2]\cdot 0.67(C_2H_5NO_2)$	16.69	22.67	6314.9	ZZZUXO		
$[Ni(4\text{-}MePy)_4(NCS)_2]\cdot 0.53(CH_4O)$	16.72	22.73	6354.4	ZZZUXQ		
$[Ni(4\text{-}MePy)_4(NCS)_2]\cdot 0.69p\text{-}DCB$	16.74	22.76	6376.3	ZZZUXS		
$[Co(4\text{-}MePy)_4(NCS)_2]\cdot 0.67NB$	16.73	22.97	6429.1	ZZZUXU		
$[Co(4\text{-}MePy)_4(NCS)_2]\cdot 0.67(C_2H_5NO_2)$	16.53	22.73	6210.8	ZZZUXY		
$[Co(4\text{-}MePy)_4(NCS)_2]\cdot 0.57C_6H_6$	16.68	23.14	6438.1	ZZZUYI		
$[Ni(4\text{-}MePy)_4(NCS)_2]$	16.74	22.66	6349.9	ICMPNI	1972	2
$[Ni(4\text{-}MePy)_4(NCS)_2]\cdot PX$	16.81	22.41	6332.5	QQQGKA	1974	3
$[Ni(4\text{-}MePy)_4(NCS)_2]\cdot PX$	16.98	23.62	6810.1	BAPZAT	1981	4
$[Ni(4\text{-}MePy)_4(NCS)_2]\cdot MX$	17.28	23.87	7127.5	BAPZEX		
$[Ni(4\text{-}MePy)_4(NCS)_2]\cdot 2MeOH$	16.99	22.29	6434.2	BAPZIB		
$[Ni(4\text{-}MePy)_4(NCS)_2]\cdot p\text{-}cymene$	17.11	23.84	6974.3	BUJPEB	1983	5
$[Fe(4\text{-}MePy)_4(NCS)_2]\cdot C_6H_6$	17.08	23.66	6902.3	VEVKEM	1990	6
$[Fe(4\text{-}MePy)_4(NCS)_2]\cdot MX$	17.17	24.02	7081.3	VEVKOW		
$[Fe(4\text{-}MePy)_4(NCS)_2]\cdot PX$	17.12	23.93	7013.8	VEVKUC		
$[Ni(4\text{-}MePy)_4(NCS)_2]\cdot 1.5C_4H_4O$	16.85	22.99	6527.4	RUDWAO	1996	7
$[Ni(4\text{-}MePy)_4(NCS)_2]\cdot 0.5C_4H_8O$	16.70	22.71	6333.6	RUDWES		
$[Ni(4\text{-}MePy)_4(NCS)_2]\cdot 0.88C_6H_6$	16.82	23.12	6540.9	RUDWIW		
$[Ni(4\text{-}MePy)_4(NCS)_2]\cdot 1.2CH_2Cl_2$	17.09	22.46	6559.9	RUDWOC		
$[Ni(4\text{-}MePy)_4(NCS)_2]\cdot 0.4CH_2Cl_2$	16.59	22.61	6222.9	RUDWUI		
$[Ni(4\text{-}MePy)_4(NCS)_2]\cdot 0.5C_3H_8O_2$	16.74	22.46	6293.5	RUDXAP		
$[Ni(4\text{-}MePy)_4(NCS)_2]$	16.64	22.67	6274.1	ICMPNI02	2001	8
$[Fe(4\text{-}MePy)_4(NCS)_2]\cdot 0.25p\text{-}MePy$	17.03	23.38	6779.8	XIHHAX		
$[Co(4\text{-}MePy)_4(NCS)_2]\cdot 0.25p\text{-}MePy$	16.84	22.82	6470.7	XIHHEB		
$[Ni(4\text{-}MePy)_4(NCS)_2]$	16.66	22.70	6299.4	ICMPNI04	2004	9
$[Ni(4\text{-}MePy)_4(NCS)_2]$	16.60	22.61	6228.2	ICMPNI05		
$[Ni(4\text{-}MePy)_4(NCS)_2]\cdot 0.94C_6H_6$	16.86	23.10	6563.8	ZZZUXK01		
$[Ni(4\text{-}MePy)_4(NCS)_2]\cdot xG$	16.68	22.63	6297.5	EMEHUA	2010	10

Table S2. Crystallographic information of the three phases of $[Ni(4\text{-}MePy)_4(NCS)_2]$.

	Closed **α** phase	PX-loaded **β** phase	empty-open **β′** phase
refcode	ICMPNI03	BAPZAT	ICMPNI04
Formula	$Ni(C_6H_7N)_4(NCS)_2$	$Ni(C_6H_7N)_4(NCS)_2\cdot C_8H_{10}$	$Ni(C_6H_7N)_4(NCS)_2$
Formula weight	547.4	653.4	547.4
Crystal system	Monoclinic	Tetragonal	Tetragonal

Space group	$P2_1/c$	$I4_1/a$	$I4_1/a$
a/Å	19.226	16.98	16.657
b/Å	9.749	16.98	16.657
c/Å	16.791	23.62	22.704
β/°	113.62	90	90
Volume/Å^3	2883.54	6810.13	6299.35
Z	4	8	8

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