

## Supporting Information

# Modulating Guest Binding in Sulfonylcalixarene- Based Metal-Organic Supercontainers

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## General Methods

Unless otherwise noted, starting materials and solvents were obtained from commercial suppliers (Fisher Scientific, TCI, Alfa Aesar, Cambridge Isotope Laboratories, Inc., etc.) and used without further purification. *p-tert*-Butylsulfonylcalix[4]arene (TBSC)<sup>1,2</sup> was synthesized as described in the literature. UV-Vis studies were done on a Varian Cary 5000 UV-Vis-NIR spectrophotometer at room temperature. Mass spectra were collected using a Varian 500-MS Ion Trap Mass Spectrometer. A CE-440 elemental analyzer (EAI Exeter Analytical Inc., North Chelmsford, Massachusetts) was used to determine the weight fractions of carbon, hydrogen and nitrogen. Elemental analysis results were based on the average of two or more trials for each sample. Thermogravimetric analysis (TGA) was performed at a scan speed of 2 °C/min under a stream of nitrogen on a TA Instruments Q600 SDT. Typical sample size ranged from ~5-10mg. Gas and vapor adsorption isotherms were measured using a Micromeritics ASAP2020 instrument based on a volumetric method. Samples were typically washed with methanol and pre-dried on a Schlenk line at 120 °C for 8 hrs before transferred to pre-weighed analysis tubes which were then capped with seal frits. The samples were degassed under dynamic vacuum (< 6 μmHg) at 105 °C for ~24-48 h until the outgas rates were lower than 5 μmHg/min. The analysis tubes containing the evacuated samples were weighed again to determine the sample weights (typically ~100 mg for most samples) before transferred back to the analysis port of the instrument. The H<sub>2</sub>, N<sub>2</sub> and O<sub>2</sub> isotherms were measured at 77 K in a liquid N<sub>2</sub> bath using ultra high pure (UHP) grade gases (99.99%), the CO<sub>2</sub> isotherms were measured at 196 K in a dry ice/isopropanol bath using ultra high pure (UHP) grade CO<sub>2</sub> gas (99.99%), and the MeOH and benzene isotherms were measured at 293 K in a water bath using the respective high purity vapor source (99.9%).

**X-Ray Crystallography:** X-ray single-crystal diffraction data were collected at 100 K using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) on a Bruker CCD APEXII diffractometer. The collected frames were processed with the software SAINT.<sup>3</sup> The data were corrected for absorption using the SADABS program.<sup>4</sup> The structure was solved by the Direct methods (SHELX97)<sup>5</sup> in conjunction with standard difference Fourier techniques and subsequently refined by full-matrix least-squares analyses on  $F^2$ . Hydrogen atoms were generated in their idealized positions and all non-hydrogen atoms were refined anisotropically. The electron count due to disordering solvents in the void space of the crystals was calculated using the program SQUEEZE in PLATON software package.<sup>6</sup> The crystals had weak diffractions, especially at higher Bragg angles. The situation did not improve even with very long exposure time. Owing to the disordering of the solvent molecules and/or *t*-butyl groups in the structures, a number of restraints, such as DFIX, SIMU, DELU and ISOR, were applied to control the refinement. The higher R-factor values and residual density maxima of **2-Ni** might be due to the weak high-angle diffractions as well as the disordering of solvent molecules. Nevertheless, the refined structures have a data-to-parameter ratio of 8-12. Weak diffractions and high disordering are typical for supramolecular structures with large unit cells and open voids. Therefore we believe our structure refinements are reasonable and reliable. CCDC 898825, 898826 and 898832 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

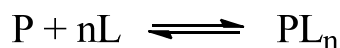
**Solid-Liquid Dye Adsorption Experiments:** The MOSC samples were dried on a Schlenk line at 120 °C for 10 hrs prior to use. An aqueous stock solution of methylene blue (MB) was prepared by dissolving MB in deionized water. A precisely weighted amount of the MOSCs (~ 4 mg) was placed in a diluted MB solution (100 mL) and the suspension was well mixed with

stirring at room temperature. The concentrations of the MB solutions were determined on the basis of the absorbance at 664 nm using a calibration curve. The UV-Vis spectra of the solutions were monitored at different time intervals to determine the concentration of the remaining (i.e., unadsorbed) MB.

**Job Plot Experiments.**<sup>7</sup> For the Job plot experiments, MOSC ( $1 \times 10^{-5}$  mol/L) in  $\text{CHCl}_3$  and methylene blue (MB) ( $1 \times 10^{-5}$  mol/L) in  $\text{CHCl}_3$  were prepared as stock solutions. These stock solutions were then used to prepare a number of mixture solutions (4.0 mL) with different MOSC/MB molar ratios. For each mixture solution, the total molar concentration of MOSC and MB was maintained constant. UV-Vis spectra of the solutions were recorded on the Cary 5000 spectrophotometer.

**Solution UV-Vis Titration Experiments:** A stock solution of methylene blue (MB) was prepared in DMF at a concentration of  $\sim 5 \times 10^{-6}$  mol/L. An accurately known mass of the MOSC sample was dissolved in 10.00 mL of the same MB stock solution to yield a solution that contained the MOSC 20~100 times as much as MB, which also ensured that MB concentration would remain constant during titration. 2.00 ml of the MB stock solution was then placed in a 10-mm quartz cell, to which 0.01 to 2 ml of the MOSC solution were added in successive portions. After each addition, the cell was capped and inverted to ensure the components were fully mixed and equilibration was reached, and UV-Vis spectrum of the solution was then recorded on the spectrophotometer. The titrations were done in this manner to ensure quantitative measurements of the binding events, as the absorption band of MB at 665 nm does not overlap with the absorbance of the MOSCs; titrating MB to a MOSC solution will be complicated by a significant overlap of the MOSC absorbance at ca. 350 nm with the second absorption band of MB (at ca. 294 nm with a shoulder at 330 nm).

**Calculation of Binding Constants from UV-Vis Titration Data<sup>8</sup>:** Binding of the ligand (L) and receptor (P) can be represented as following (in our study, L = **1-Ni** or **2-Ni**, and P = MB):



The association constant  $K_a$  and dissociation constant  $K_d$  of the binding can be defined as in

Equation 1:

$$K_a = \frac{[PL_n]}{[P][L]^n} = \frac{1}{K_d} \quad (1)$$

[P] and [L] are concentrations of free P and free L while  $[PL_n]$  is the concentration of the bound complex. The total concentrations of P and L in solution are  $[P]_0$  and  $[L]_0$ , respectively.

Therefore, we have:

$$[L]_0 = [L] + n[PL_n] \quad (2)$$

$$[P]_0 = [P] + [PL_n] \quad (3)$$

An experimentally accessible parameter,  $\alpha$ , can be defined as the ratio of the complex concentration at any concentration of L versus the total concentration of P ( $[P]_0$ ).

$$\alpha = \frac{[PL_n]}{[P]_0} = \frac{[PL_n]}{[P] + [PL_n]} = \frac{K_a[P][L]^n}{[P] + K_a[P][L]^n} = \frac{K_a[L]^n}{1 + K_a[L]^n} \quad (4)$$

The change in physical properties, such as absorbance ( $\Delta A$ ), fluorescence ( $\Delta F$ ), etc., upon formation of a complex can be used to determine  $K_a$  if the change in physical properties is directly proportional to the concentration of the complex:

$$\frac{\Delta A}{\Delta A_{max}} = \alpha \quad (5)$$

Equation (4) and (5) can be rewritten as:

$$\alpha = \frac{\Delta A}{\Delta A_{max}} = \frac{K_a[L]^n}{1+K_a[L]^n} = \frac{[L]^n}{K_d+[L]^n} \quad (6)$$

When the initial concentration of the receptor ( $[P]_0$ ) is in the range of  $K_d$ , the value of  $[L]$  is close to the value of  $[L]_0$  (i.e.,  $[L]_0 \approx [L]$ ). This allows a simple approximation of Equation 6 by substituting  $[L]$  with  $[L]_0$  and modifying the equation to:

$$\alpha = \frac{\Delta A}{\Delta A_{max}} = \frac{K_a[L]_0^n}{1+K_a[L]_0^n} = \frac{[L]_0^n}{(1/K_a)+[L]_0^n} \quad (7)$$

A plot of  $\Delta A$  against  $[L]_0$  can be used to estimate  $\Delta A_{max}$  and  $K_d$ . The titration data (in this study,  $[P]_0 = [\text{MB}]$ ,  $[L]_0 = [\mathbf{1-Ni}]$  or  $[\mathbf{2-Ni}]$ ) were fit to this model using the non-linear regression method within the Origin 9 software.

## Synthesis

**1-Ni:**  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (72.7 mg, 0.25 mmol), 1,3-benzenedicarboxylic acid (1,3-BDC) (18.4 mg, 0.11 mmol) and TBSC (42.5 mg, 0.05 mmol) were dissolved in 10 mL of *N,N*-dimethylformamide (DMF) and 5 mL of methanol in a scintillation vial (20 mL capacity). The vial was placed in a sand bath, which was transferred to a programmable oven and heated at a rate of 0.5 °C/min from 35 to 100 °C. The temperature was held at 100 °C for 24 h before the oven was cooled at a rate of 0.2 °C/min to a final temperature of 35 °C. Green crystals of **1-Ni** were isolated by washing with methanol and dried in the air to give 50.5mg of the as-synthesized material.

**1-Co:**  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (14.6 mg, 0.05 mmol), 1,3-BDC (3.7 mg, 0.022 mmol) and TBSC (8.5 mg, 0.01 mmol) were dissolved in 2 mL of DMF and 1 mL of methanol in a dram vial (4 mL capacity). The vial was placed in a sand bath, which was transferred to a programmable oven and

heated at a rate of 0.5 °C/min from 35 to 100 °C. The temperature was held at 100 °C for 24 h before the oven was cooled at a rate of 0.2 °C/min to a final temperature of 35 °C. Pink crystals of **1-Co** that formed in 3 days were isolated by washing with methanol and dried in the air to give 9.2 mg of the as-synthesized material.

**2-Ni:** Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (146.1 mg, 0.50 mmol), 5-sulfo-1,3-benzenedicarboxylic acid monolithium salt (5-SO<sub>3</sub>-1,3-BDC) (55.5 mg, 0.22 mmol) and TBSC (85.0 mg, 0.10 mmol) were dissolved in 10 mL of DMF in a scintillation vial (20 mL capacity). The vial was placed in a sand bath, which was transferred to a programmable oven and heated at a rate of 0.5 °C/min from 35 to 100 °C. The temperature was held at 100 °C for 24 h before the oven was cooled at a rate of 0.2 °C/min to a final temperature of 35 °C. Green crystals of **2-Ni** were isolated by washing with methanol and dried in the air to give 62.5 mg of the as-synthesized material.

**Table S1.** Crystallographic Data for Compounds **1-Ni**, **1-Co** and **2-Ni**

	<b>1-Ni</b>	<b>1-Co</b>	<b>2-Ni</b>
Empirical formula	C <sub>224</sub> H <sub>216</sub> Ni <sub>16</sub> O <sub>84</sub> S <sub>16</sub>	C <sub>224</sub> H <sub>216</sub> Co <sub>16</sub> O <sub>84</sub> S <sub>16</sub>	C <sub>260</sub> H <sub>316</sub> Ni <sub>12</sub> Ni <sub>20</sub> O <sub>132</sub> S <sub>24</sub>
Formula weight	5704.29	5707.81	7664.89
Temperature (K)	100	100	100(2) K
Crystal system	Triclinic	Triclinic	Triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	18.4577(11)	18.520(3)	21.147(4)
<i>b</i> (Å)	19.1682(11)	19.184(3)	26.432(5)
<i>c</i> (Å)	25.4945(15)	25.574(4)	28.226(5)
$\alpha$ (°)	90.1750(10)	90.610(2)	107.250(2)
$\beta$ (°)	99.6530(10)	99.342(2)	97.364(2)
$\gamma$ (°)	91.1890(10)	90.718(2)	92.921(2)
<i>V</i> (Å <sup>3</sup> )	8890.2(9)	8964(2)	14877(5)
<i>Z</i>	1	1	1
D(calcd) (g cm <sup>-3</sup> )	1.064	1.057	0.856
$\mu$ (Mo <i>K</i> $\alpha$ ) (mm <sup>-1</sup> )	0.979	0.871	0.752
<i>F</i> (000)	2928	2920	3960
$\theta$ range (°)	1.81 - 18.02	1.80 - 18.72	1.68 - 24.07
Limiting indices	-16 ≤ <i>h</i> ≤ 16	-16 ≤ <i>h</i> ≤ 16	-24 ≤ <i>h</i> ≤ 24
	-16 ≤ <i>k</i> ≤ 16	-17 ≤ <i>k</i> ≤ 17	-30 ≤ <i>k</i> ≤ 30
	-22 ≤ <i>l</i> ≤ 22	-23 ≤ <i>l</i> ≤ 22	-32 ≤ <i>l</i> ≤ 32
Reflections collected / unique	42305 / 12265	45705 / 13729	114427 / 46225
	[ <i>R</i> <sub>int</sub> = 0.0382]	[ <i>R</i> <sub>int</sub> = 0.0477]	[ <i>R</i> <sub>int</sub> = 0.0450]
Data / restraints / parameters	12265 / 178 / 1526	13729 / 156 / 1519	46225 / 166 / 1990
GOF	1.065	0.970	1.253
<i>R</i> <sub>1</sub> ( <i>I</i> > 2σ( <i>I</i> ))	0.0501	0.0747	0.1972
<i>wR</i> <sub>2</sub> ( <i>I</i> > 2σ( <i>I</i> ))	0.1514	0.2183	0.5824
<i>R</i> <sub>1</sub> (all data)	0.0611	0.0926	0.2202
<i>wR</i> <sub>2</sub> (all data)	0.1591	0.2406	0.6248
$\Delta\rho$ / e Å <sup>-3</sup>	1.636, -0.681	1.376, -0.932	5.055, -1.518

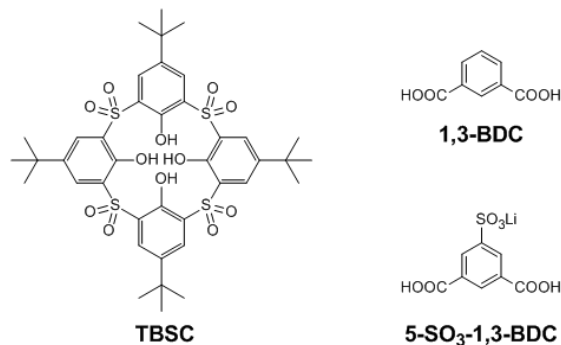


**Table S2.** Elemental analysis results of **1-Ni** and **2-Ni**

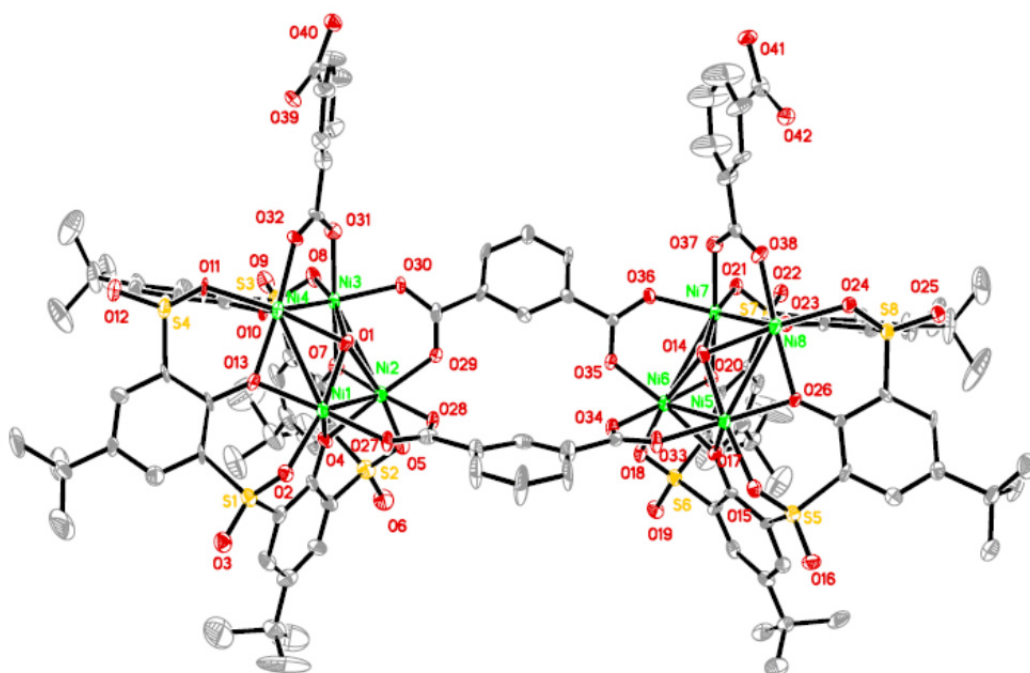
	<b>1-Ni</b>		<b>2-Ni</b>	
	As-synthesized	As-synthesized	Activated	MB adsorbed
C (%)	45.07 ± 0.39	38.15 ± 0.10	37.57 ± 0.08	49.60 ± 0.09
H (%)	5.12 ± 0.07	5.45 ± 0.06	4.25 ± 0.06	5.19 ± 0.29
N (%)	2.86 ± 0.03	4.23 ± 0.02	1.74 ± 0.02	4.25 ± 0.02

**Table S3.** Comparison of experimental and calculated exact mass data of **1-Ni** and **2-Ni**

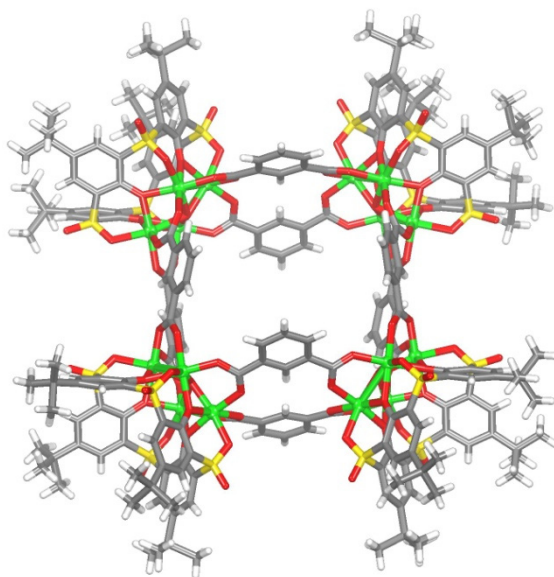
Compound	Fragment	Calculated	Experimental
<b>1-Ni</b>	$[M+H_2O-4H]^{4-}$ $C_{224}H_{214}Ni_{16}O_{85}S_{16}^{4-}$	1428.9	1428.6
	$[M+7DMF+H_2O]^{8-}$ $C_{245}H_{259}N_7Ni_{16}O_{116}S_{24}^{8-}$	857.8	858.1
<b>2-Ni</b>	$[M+Ni(H_2O)_2]^{6-}$ $C_{224}H_{212}Ni_{17}O_{110}S_{24}^{6-}$	1071.4	1071.3
	$[M+H+Ni(H_2O)_2]^{5-}$ $C_{224}H_{213}Ni_{17}O_{110}S_{24}^{5-}$	1285.9	1285.6
	$[M+2Ni+H_2O]^{4-}$ $C_{224}H_{210}Ni_{18}O_{109}S_{24}^{4-}$	1617.3	1617.9
	$[M+2Ni+4DMF+2H_2O]^{4-}$ $C_{236}H_{240}N_4Ni_{18}O_{114}S_{24}^{4-}$	1694.6	1695.4



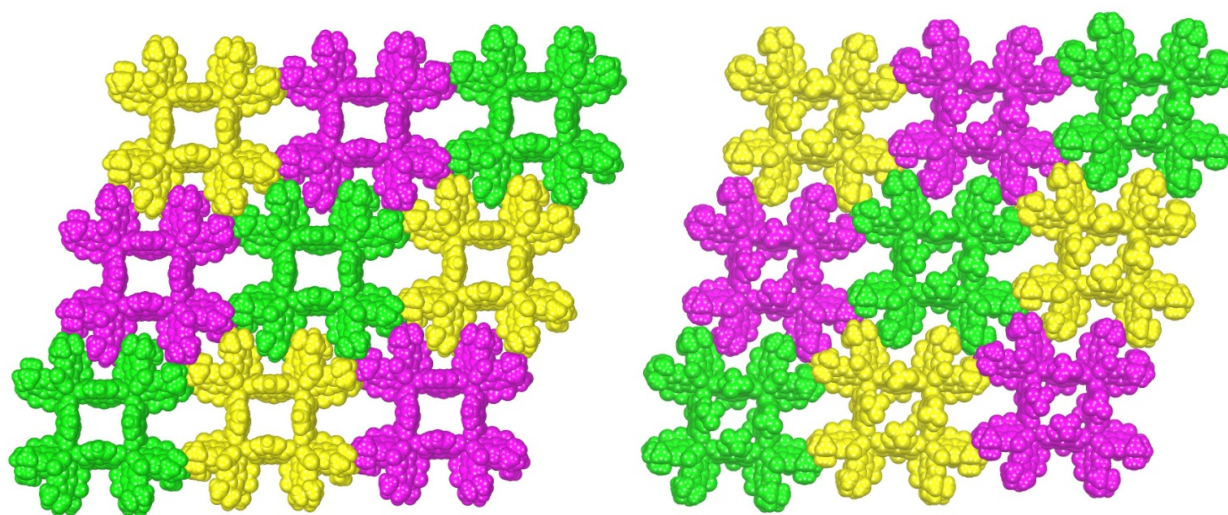
**Scheme S1.** Sulfonylcalix[4]arenes and angular dicarboxylate linkers used to construct the type III MOSCs in this study.



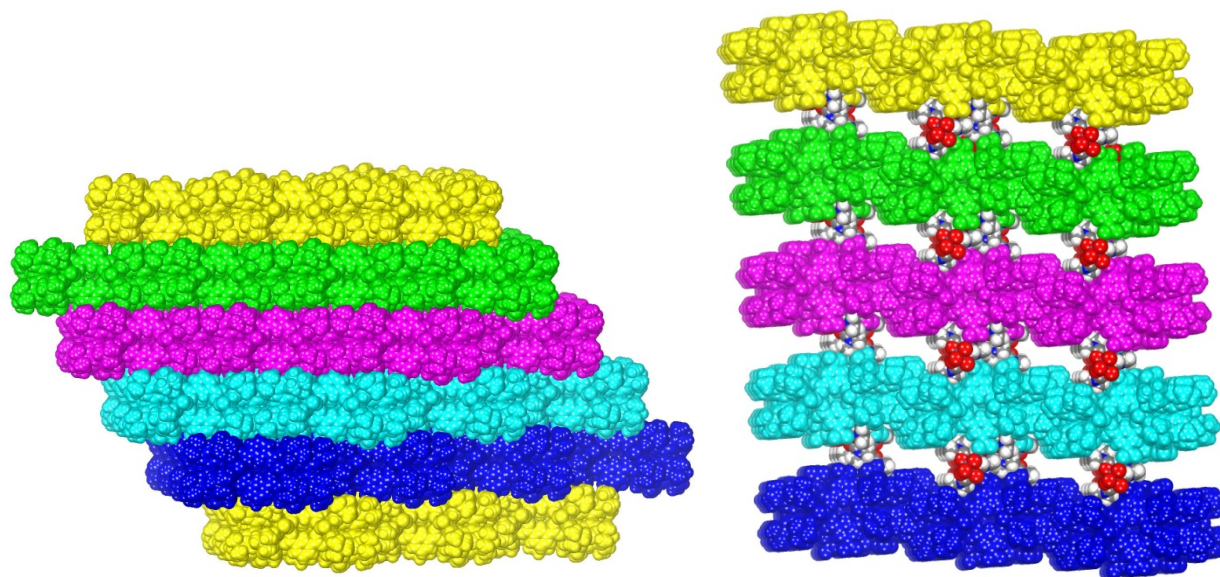
**Figure S1.** ORTEP drawing of the asymmetric unit of **1-Ni** (thermal ellipsoids with 30% probability)



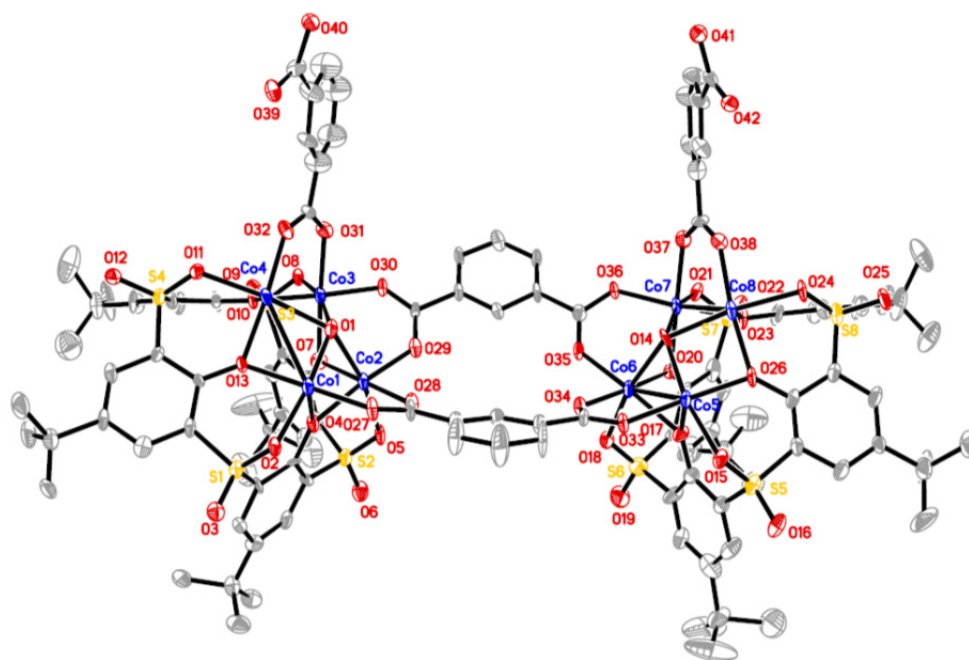
**Figure S2.** Crystal structure of **1-Ni**. Color scheme: Ni, green; S, yellow; O, red; C, grey; H, white.



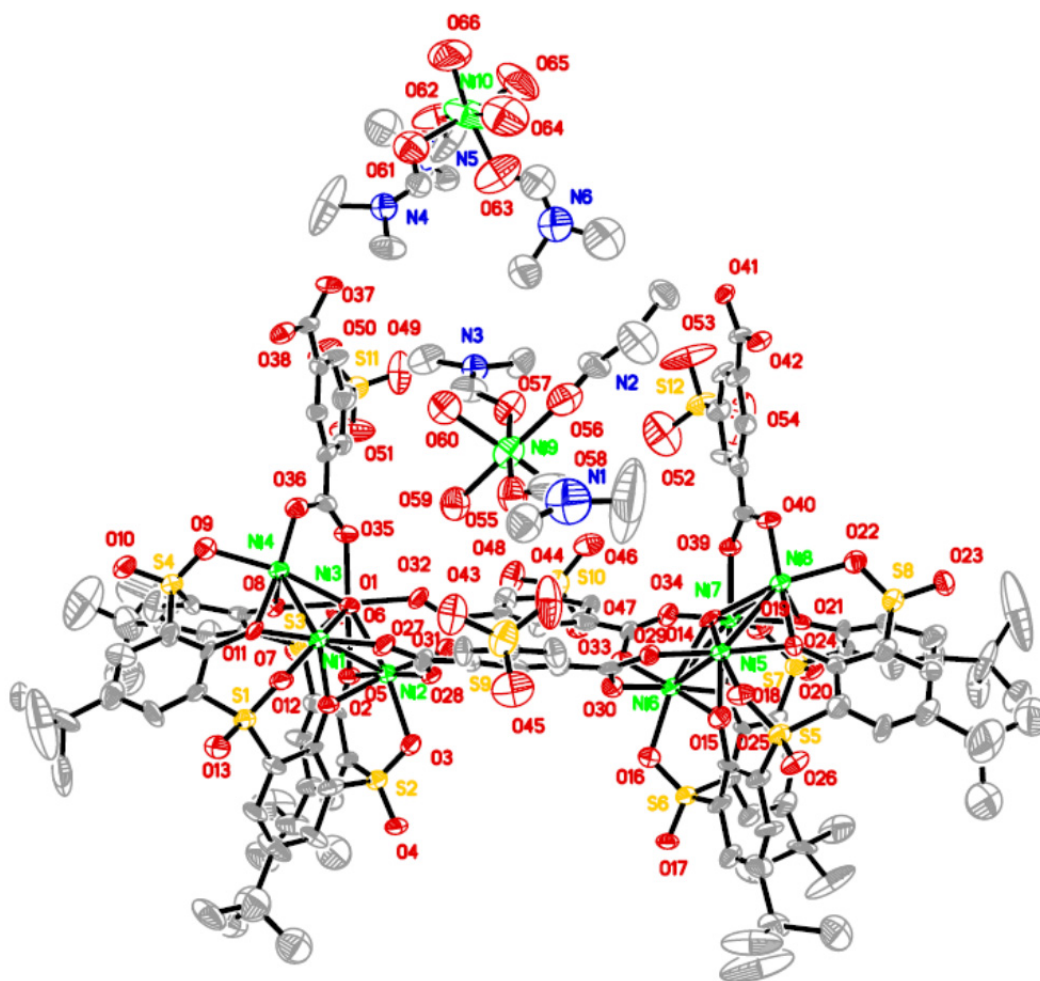
**Figure S3.** Comparison of two-dimensional packing of **1-Ni** (left) and **2-Ni** (right)



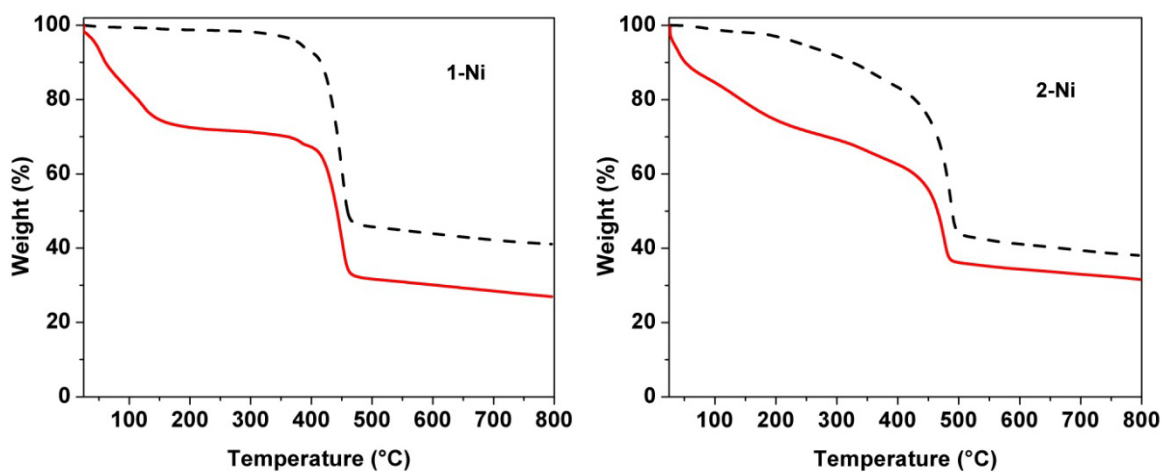
**Figure S4.** Comparison of three-dimensional packing of **1-Ni** (left) and **2-Ni** (right)



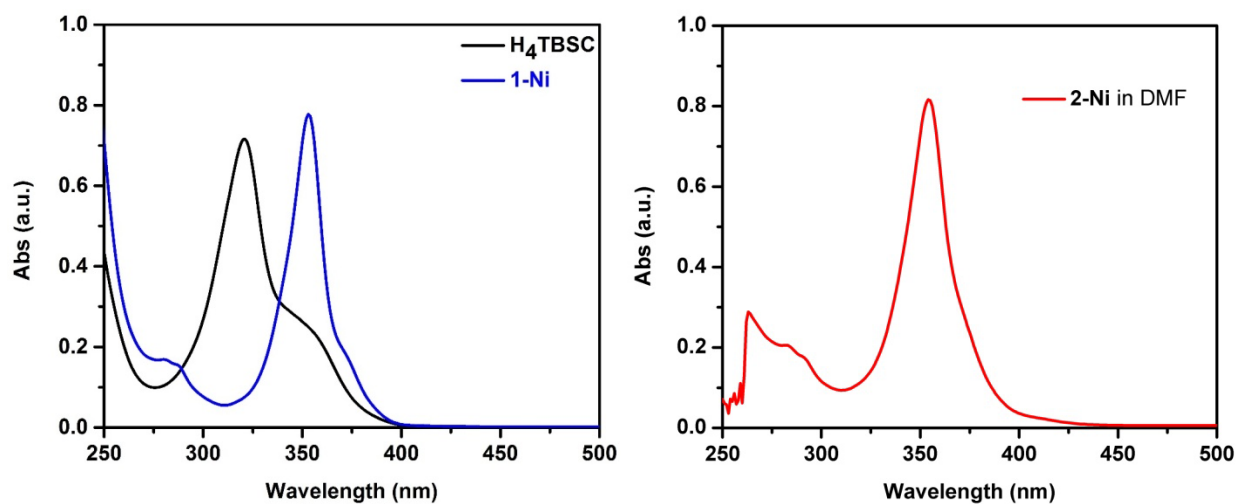
**Figure S5.** ORTEP drawing of the asymmetric unit of **1-Co** (thermal ellipsoids with 30% probability)



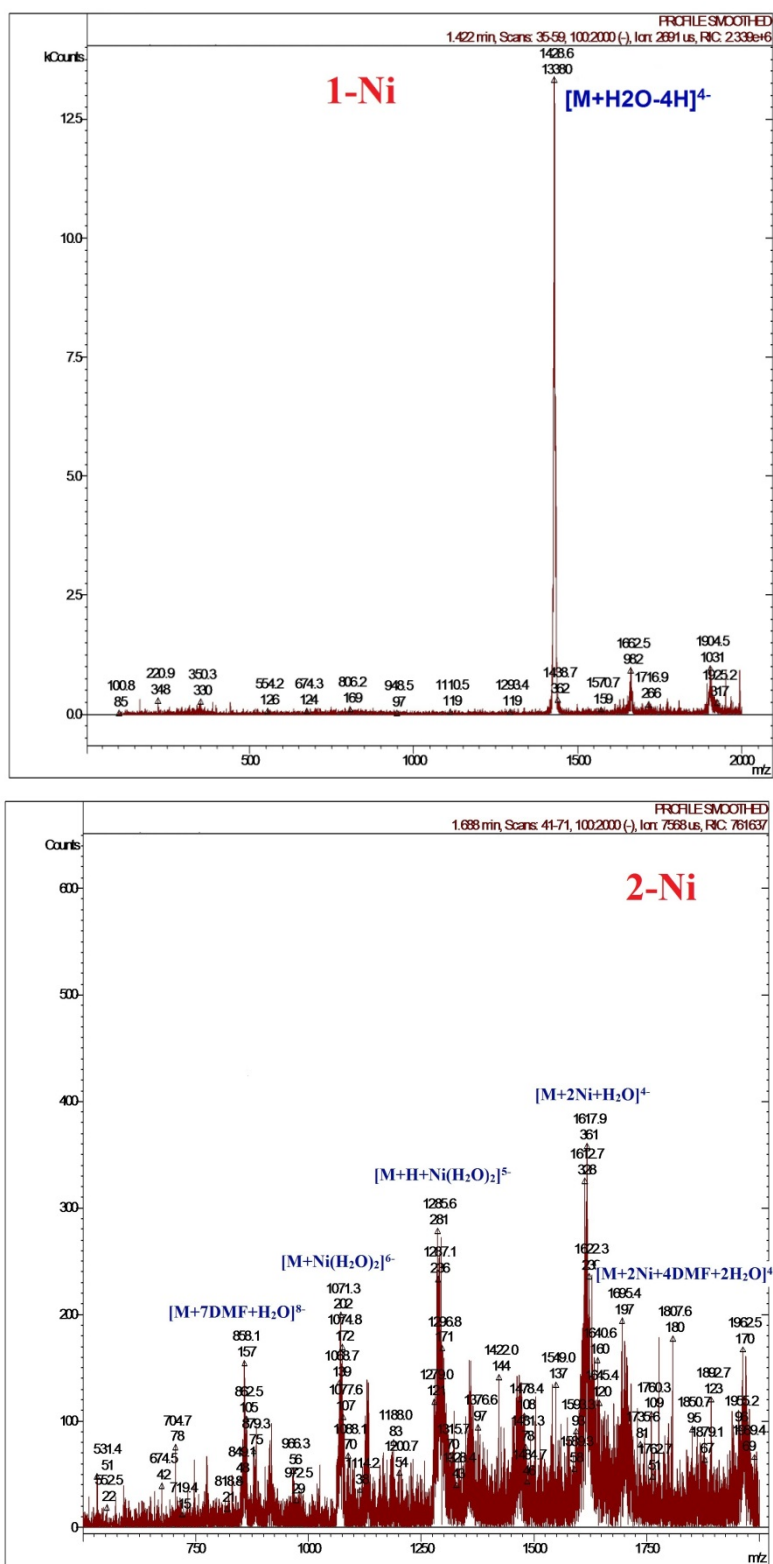
**Figure S6.** ORTEP drawing of the asymmetric unit of 2-Ni (thermal ellipsoids with 30% probability)



**Figure S7.** TGA curves of as-synthesized (red solid) and activated (black dash) **1-Ni** (left) and **2-Ni** (right).



**Figure S8.** UV-Vis spectra of H<sub>4</sub>TBSC and **1-Ni** in CHCl<sub>3</sub> (left), and **2-Ni** in DMF (right) at room temperature, indicating the structural integrity of both compounds in solution.



**Figure S9.** ESI-MS spectra of **1-Ni** (top) and **2-Ni** (bottom), indicating the structural integrity of both compounds in solution.

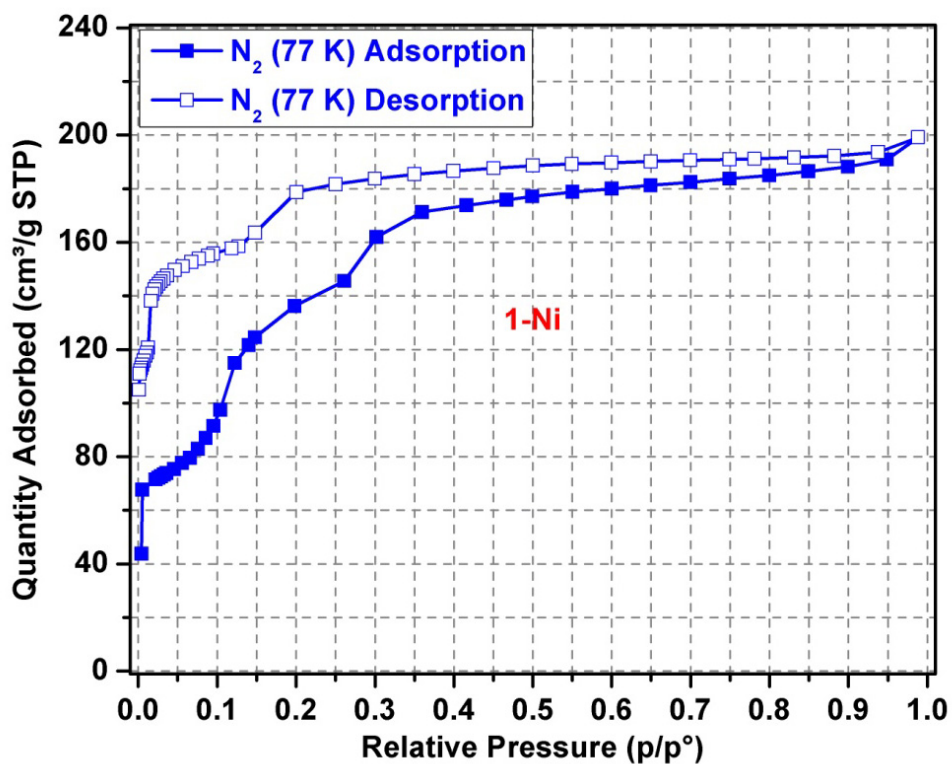


Figure S10.  $N_2$  sorption isotherm (77 K) of 1-Ni.

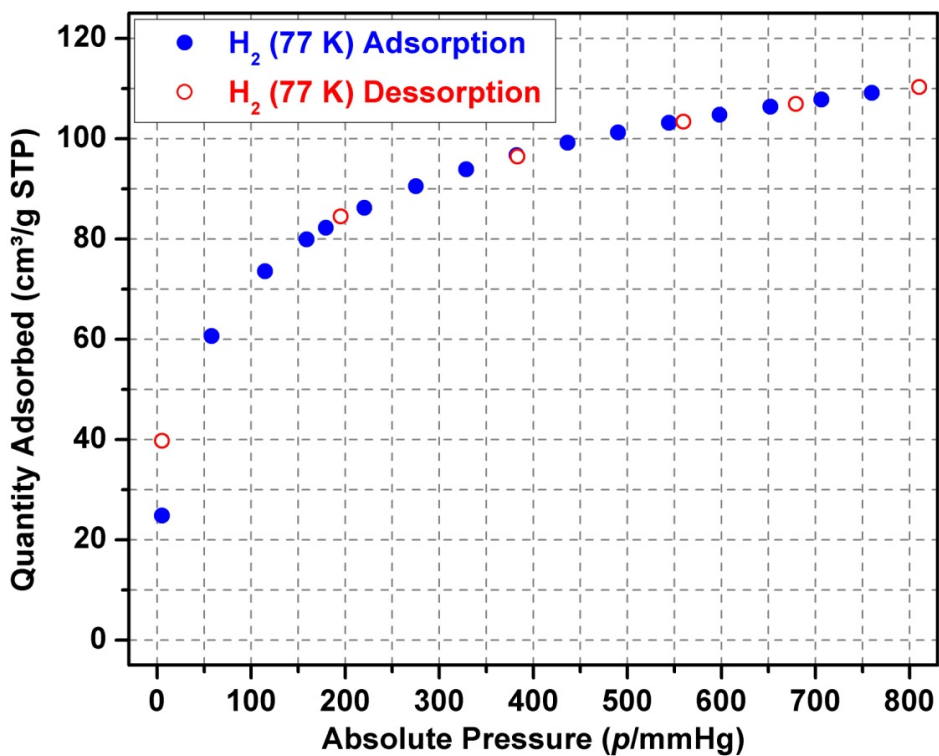
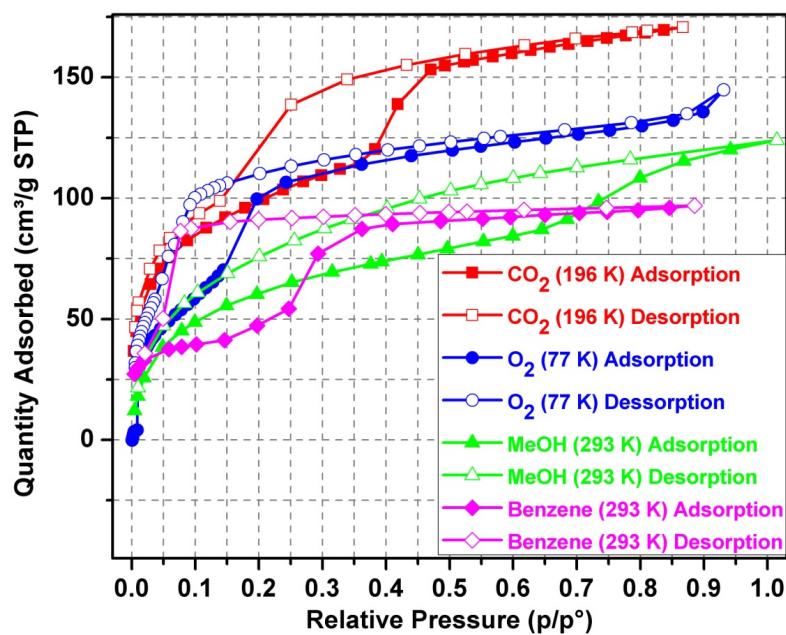
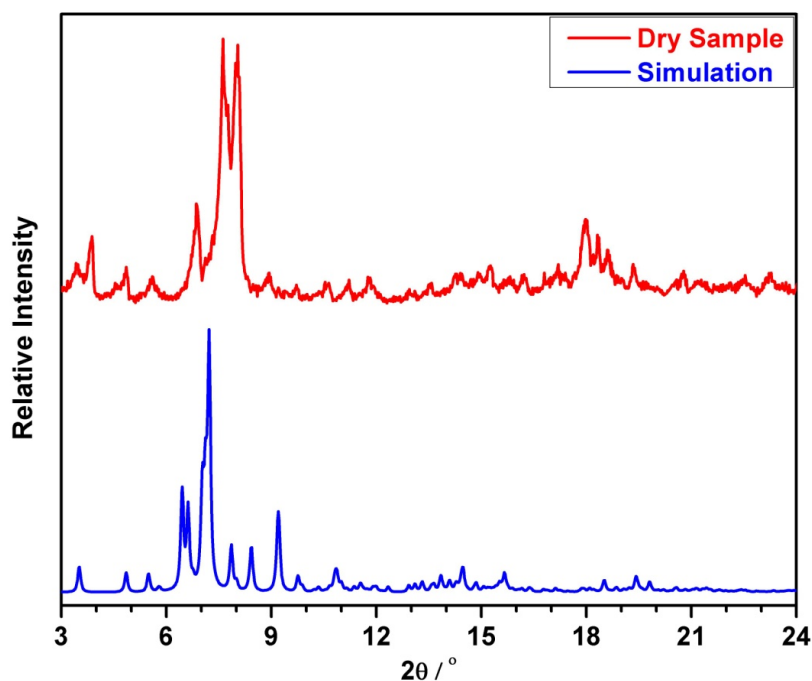


Figure S11.  $H_2$  sorption isotherm (77 K) of 1-Ni





**Figure S12.** O<sub>2</sub> (77 K), CO<sub>2</sub> (196 K), MeOH (293 K), and benzene (293 K) sorption isotherms of **1-Ni**



**Figure S13.** Simulated (blue) and experimental (red) powder X-ray diffraction patterns of **1-Ni**, the mismatch between the two suggesting possible structural rearrangement upon sample drying.

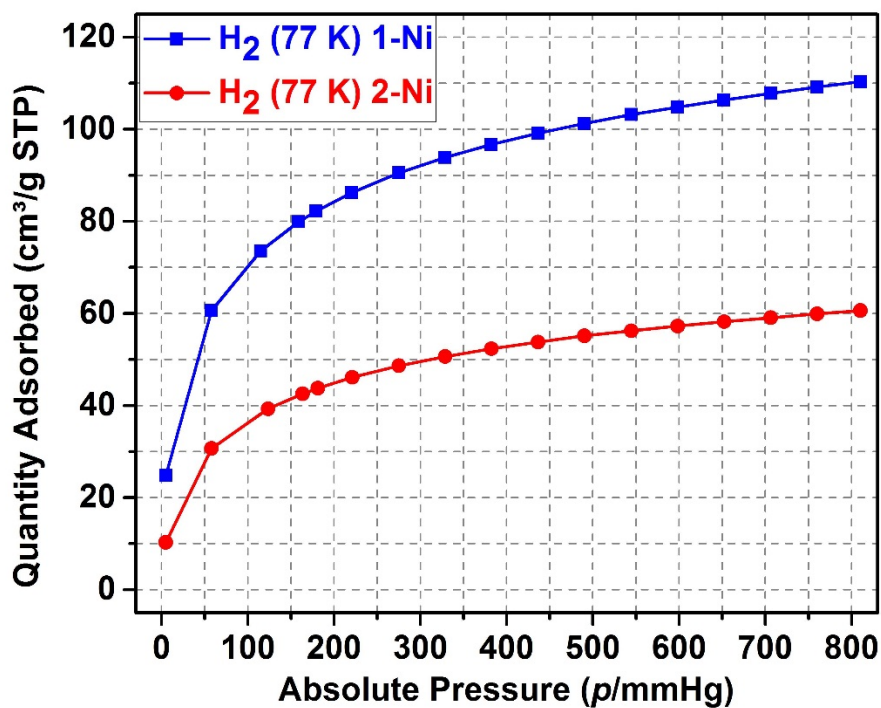


Figure S14. Comparison of H<sub>2</sub> adsorption isotherms (77 K) of 1-Ni and 2-Ni

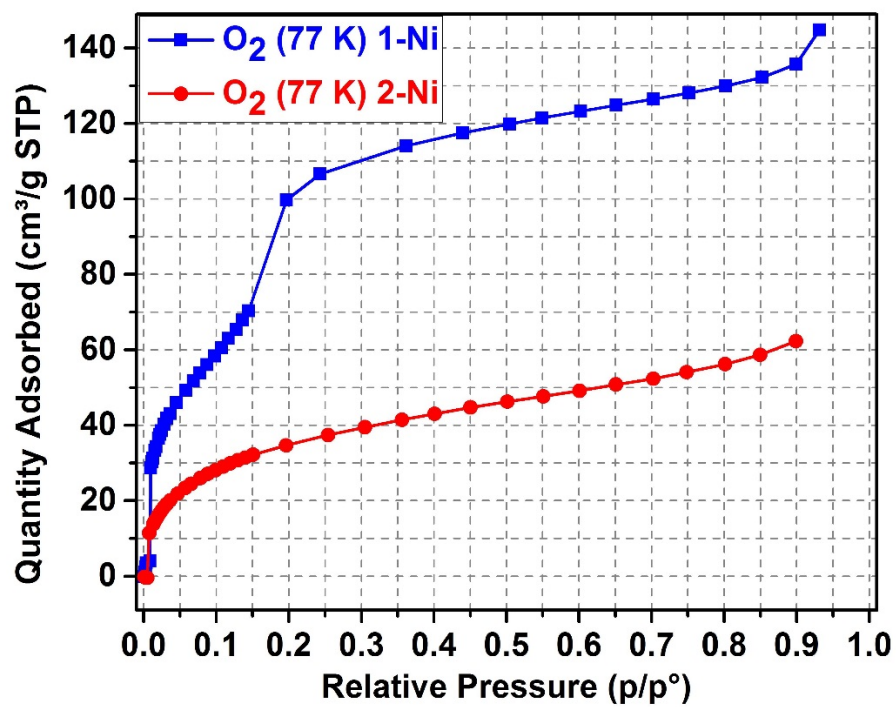


Figure S15. Comparison of O<sub>2</sub> adsorption isotherms (77 K) of 1-Ni and 2-Ni

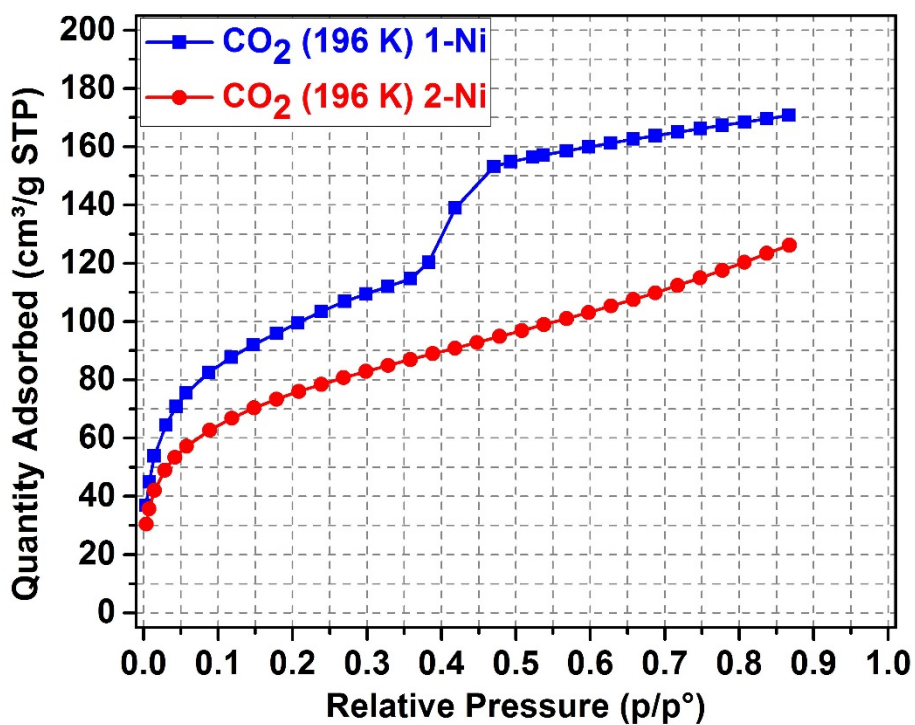


Figure S16. Comparison of CO<sub>2</sub> adsorption isotherms (196 K) of 1-Ni and 2-Ni

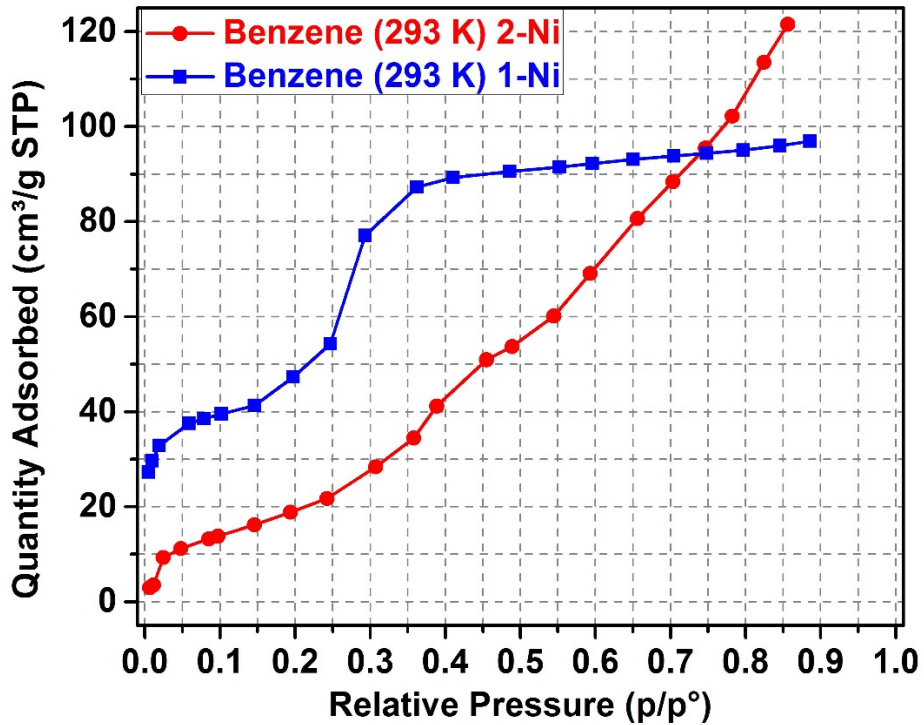
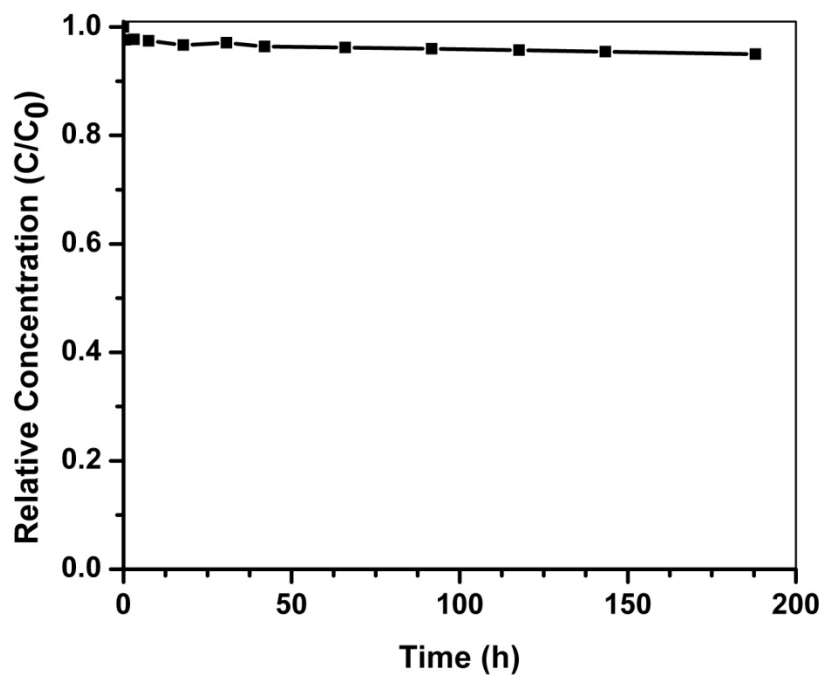
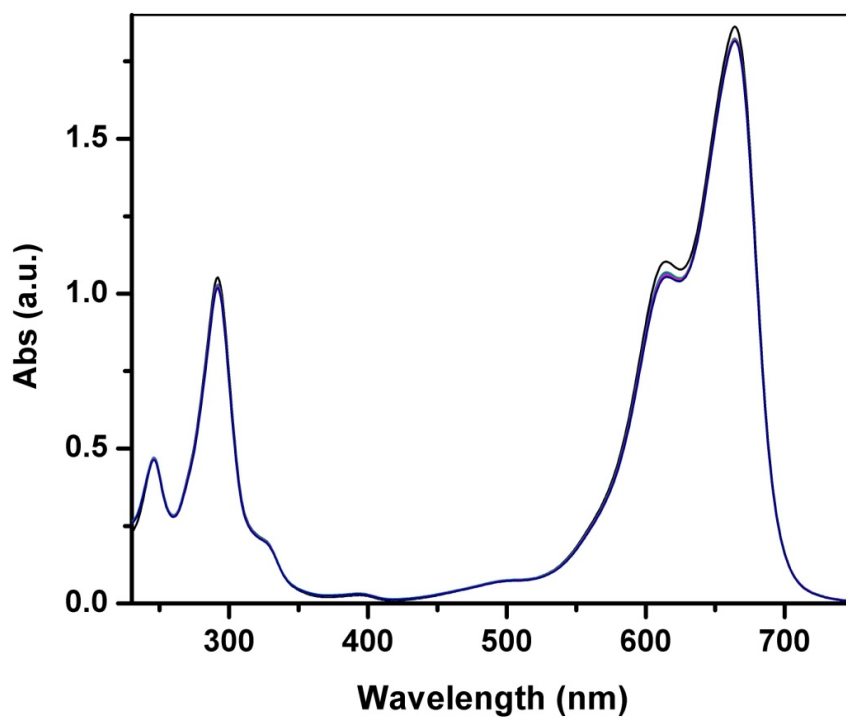


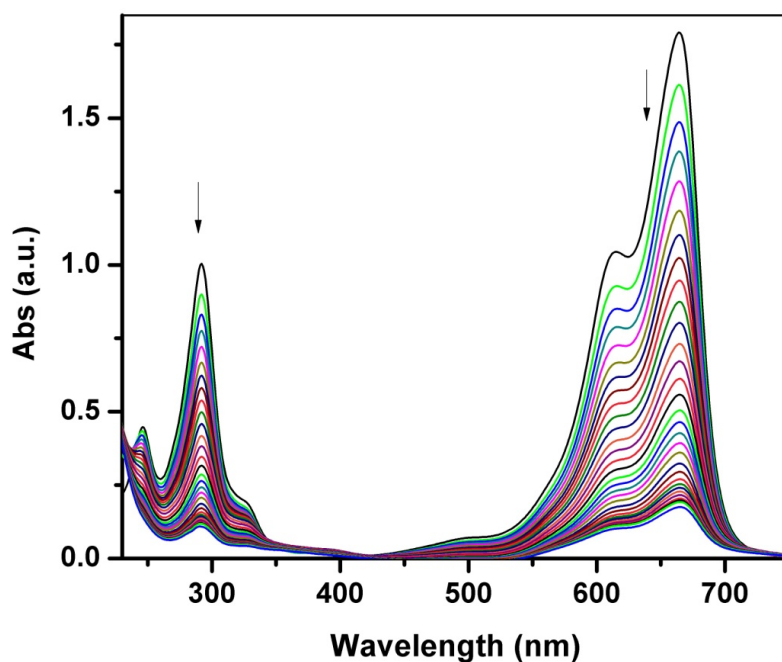
Figure S17. Comparison of benzene adsorption isotherms (293 K) of 1-Ni and 2-Ni



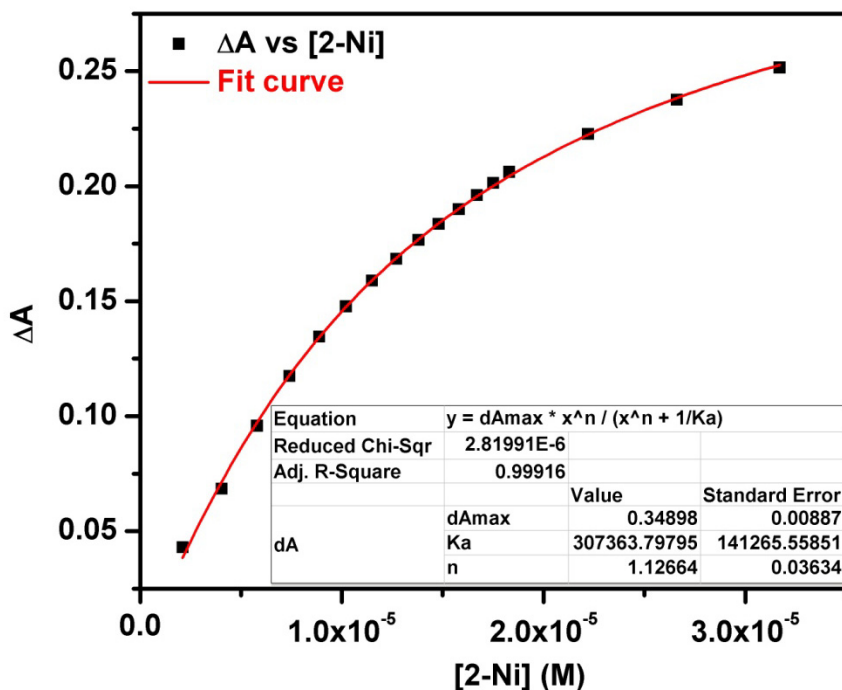
**Figure S18.** Methylene blue adsorption kinetics of **1-Ni** at the solid-liquid interface



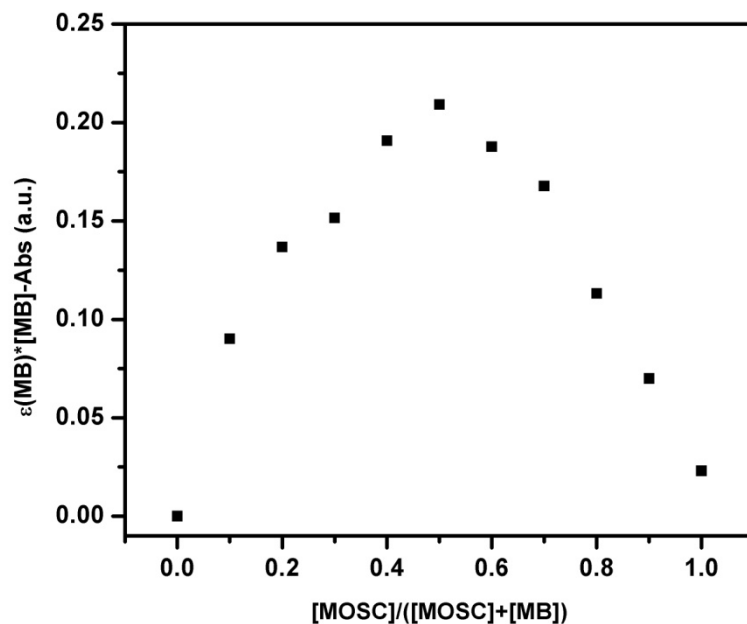
**Figure S19.** Time-dependent UV-Vis spectra of methylene blue in an aqueous solution during the adsorption by solids of **1-Ni**



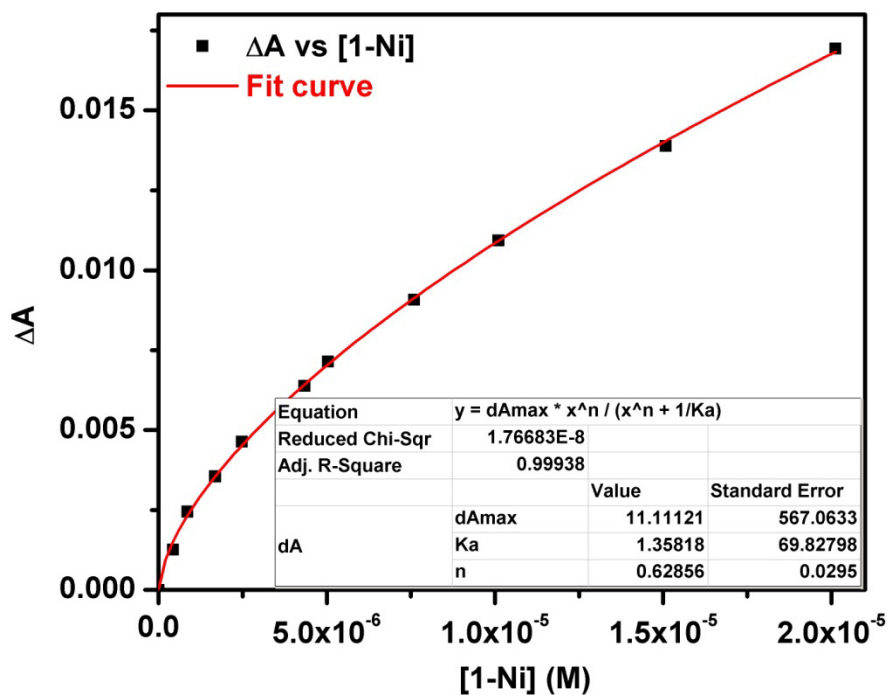
**Figure S20.** Time-dependent UV-Vis spectra of methylene blue in an aqueous solution during the adsorption by the solids of 2-Ni



**Figure S21.** Plot of  $\Delta A$  vs.  $[2-Ni](M)$  based on the methylene blue titration experiment; the best fit of the data was obtained using Equ. (7).



**Figure S22.** Job plot for the determination of the stoichiometry of 2-Ni and methylene blue binding.



**Figure S23.** Plot of  $\Delta A$  vs.  $[1\text{-Ni}](\text{M})$  based on the methylene blue titration experiment; the best fit of the data was obtained using Equ. (7).

## References

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- S1. (a) N. Iki, H. Kumagai, N. Morohashi, K. Ejima, M. Hasegawa, S. Miyanari, S. Miyano, *Tetrahedron Lett.* **1998**, *39*, 7559; (b) N. Morohashi, N. Iki, A. Sugawara, S. Miyano, *Tetrahedron*, **2001**, *57*, 5557.
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