Supplementary Information

1. Solution synthesis

1 was obtained by adding 4 equivalents of 4-PhPy to one equivalent of $Ni(NCS)_2$ in methanol (0.1 M solution). The synthesis of the inclusion compounds was attempted by adding 4 equivalents of 4-PhPy dissolved in the minimum amount of the aromatic solvent (either benzene or toluene), to one equivalent of $Ni(NCS)_2$ in methanol (0.1 M solution). Crystal growth was attempted by slow solvent evaporation.

2. Solid-vapour enclathration

The solid-vapour reactions under kinetic control were carried out by exposing about 5 mg of microcrystalline **1** to the solvent vapours in a customised microbalance that monitors weight change as a function of time under controlled conditions of temperature and pressure.
Isothermal sorption measurements for **1** were conducted in a ASAP 2020 sorption analyser.

3. Solid-liquid enclathration

The solid-liquid enclathrations were carried out by covering 5 mg of 1 with 5 ml of benzene and toluene respectively.

4. Crystallographic data

Single crystal X-ray diffraction data were collected on a Bruker Apex II Duo diffractometer employing Mo-Kα radiation. The temperature was controlled using an Oxford Cryostream cooler. Data reduction and absorption corrections were carried out using the SAINT[1] and SADABS[2,3] software packages, respectively. The structures were solved by direct methods using SHELXS-97.[4] Non-hydrogen atoms were refined anisotropically by means of full-matrix least squares calculations on F^2 using SHELXL-97[4] within the X-Seed[5] graphical user interface. Hydrogen atoms were placed on calculated positions.

Crystal data for **1bnz**: $C_{52}H_{42}N_6NiS_2$, M = 873.75, light blue plates, 0.20 × 0.07 × 0.07 mm^3, triclinic, space group P-1 (No. 2), a = 13.039(4), b = 13.178(4), c = 21.477(7) Å, α = 85.204(4), β = 79.744(4), γ = 64.519(3)°, V = 3278.1(18) $Å^3$, Z = 3, D_c = 1.328 g/cm^3, F_{000} =

1368, MoKα radiation, λ = 0.71073 Å, T = 100(2)K, $2\theta_{max}$ = 57.5º, 38688 reflections collected, 15449 unique (R_{int} = 0.1606). Final *GooF* = 0.993, *R1* = 0.1252, *wR2* = 0.2971, *R* indices based on 5396 reflections with I >2sigma(I) (refinement on F^2), 807 parameters, 48 restraints. Lp and absorption corrections applied, μ = 0.583 mm^{-1}. 9 Uiso/Uij restrained atom sites, and 48 least-squares restraints were used in the refinement to model the geometry of the guest (SIMU 0.1 and AFIX 66).

Crystal data for **1bnz2**: $C_{58}H_{48}N_6NiS_2$, M = 951.85, blue plate, 0.30 × 0.20 × 0.10 mm^3, monoclinic, space group $P2_1/c$ (No. 14), a = 18.502(2), b = 11.9483(14), c = 23.881(3) Å, β = 111.591(2)°, V = 4908.9(10) $Å^3$, Z = 4, D_c = 1.288 g/cm^3, F_{000} = 1992, MoKα radiation, λ = 0.71073 Å, T = 100(2)K, $2\theta_{max}$ = 57.8º, 29142 reflections collected, 11644 unique (R_{int} = 0.1029). Final *GooF* = 0.859, *R1* = 0.0651, *wR2* = 0.1522, *R* indices based on 5725 reflections with I >2sigma(I) (refinement on F^2), 604 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.525 mm^{-1}.

Crystal data for **1tol I**: $C_{60}H_{52}N_6NiS_2$, M = 979.91, light blue needle, 0.30 × 0.30 × 0.10 mm^3, orthorhombic, space group *Fdd*2 (No. 43), a = 43.6737(9), b = 10.2287(2), c = 22.9715(4) Å, V = 10261.9(3) $Å^3$, Z = 8, D_c = 1.269 g/cm^3, F_{000} = 4112, MoKα radiation, λ = 0.71073 Å, T = 100(2)K, $2\theta_{max}$ = 69.1º, 17282 reflections collected, 8191 unique (R_{int} = 0.0336). Final *GooF* = 1.035, *R1* = 0.0386, *wR2* = 0.0887, *R* indices based on 7131 reflections with I >2sigma(I) (refinement on F^2), 383 parameters, 1 restraint. Lp and absorption corrections applied, μ = 0.505 mm^{-1}. Absolute structure parameter = 0.375(9) (Flack, H. D. *Acta Cryst*. **1983**, *A39*, 876-881).

Crystal data for **1tol II**: $C_{30}H_{26}N_3Ni_{0.50}S$, M = 489.95, light blue plate, 0.12 × 0.08 × 0.08 mm^3, monoclinic, space group *C*2/*c* (No. 15), a = 10.620(6), b = 23.084(12), c = 22.693(12) Å, β = 99.406(8)°, V = 5488(5) $Å^3$, Z = 8, D_c = 1.186 g/cm^3, F_{000} = 2056, MoKα radiation, λ = 0.71073 Å, T = 293(2)K, $2\theta_{max}$ = 46.6º, 11777 reflections collected, 3936 unique (R_{int} = 0.0726). Final *GooF* = 1.071, *R1* = 0.0760, *wR2* = 0.2223, *R* indices based on 2447 reflections with I >2sigma(I) (refinement on F^2), 288 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.472 mm^{-1}.

5. PXRD

All diffraction patterns were recorded on a PANalytical XPERT-PRO diffractometer system using Bragg-Brentano geometry and an incident beam of Cu Kα radiation (λ = 1.5418 Å). A sheet of beryllium was used to cover the sample to avoid the evaporation of solvent during the diffraction analysis.

Time-lapsed structural analysis for the solid-vapour reaction was performed off site by collecting PXRD patterns at different times during the reaction as described at point 2.

Time-lapsed structural analysis for the solid-liquid reaction was performed *in situ* by placing about 5 mg of microcrystalline **1** on a silicon sample holder and by layering the sample with about 2 ml of toluene.

6. Figures

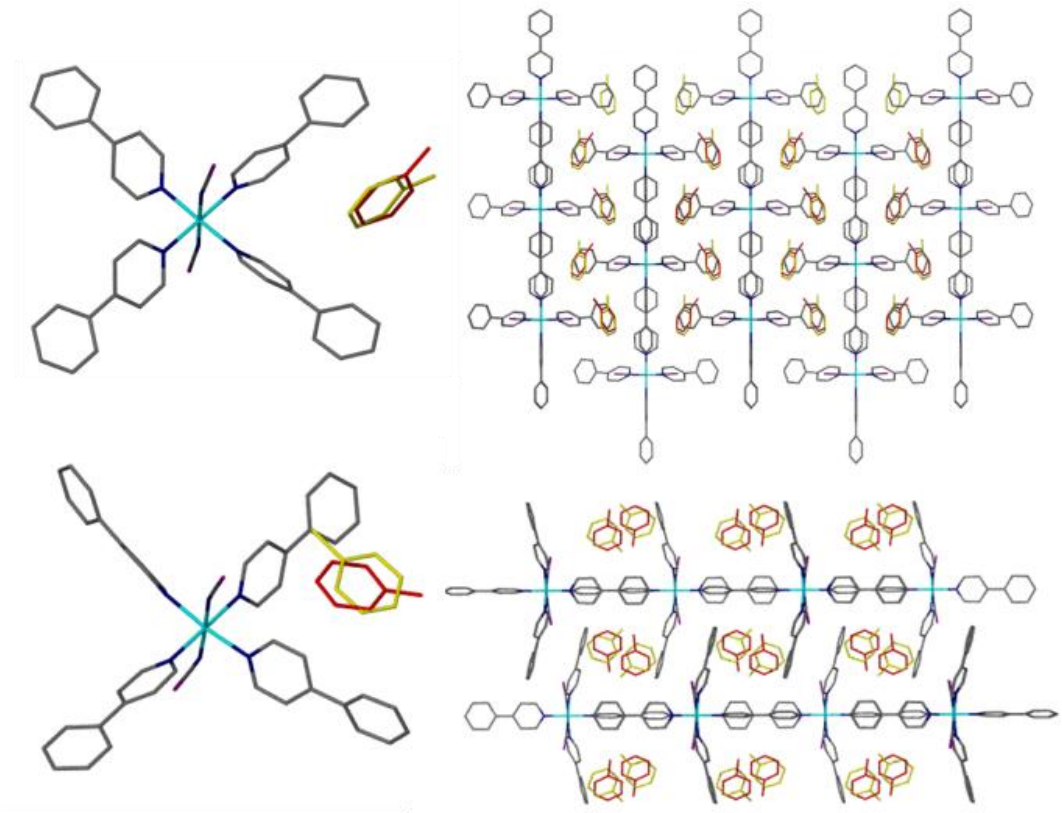

Figure 1: Molecular and unit cell structure of **1tol**: form 1 (top) and form 2 (bottom). Hydrogen atoms are omitted for clarity. The two possible position of toluene are indicated in blue and red. Thermal ellipsoids are reported for the metal complex

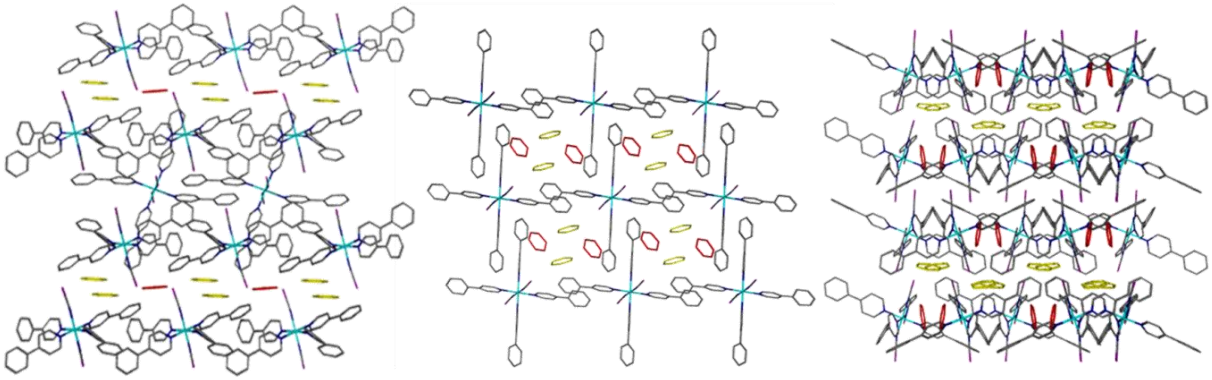

Figure 2: crystal packing of **1bnz** (left), and **1bnz4** (middle) and **bnz2** (right). Hydrogens are omitted for clarity and symmetry independent benzene molecules are coloured in red and yellow.

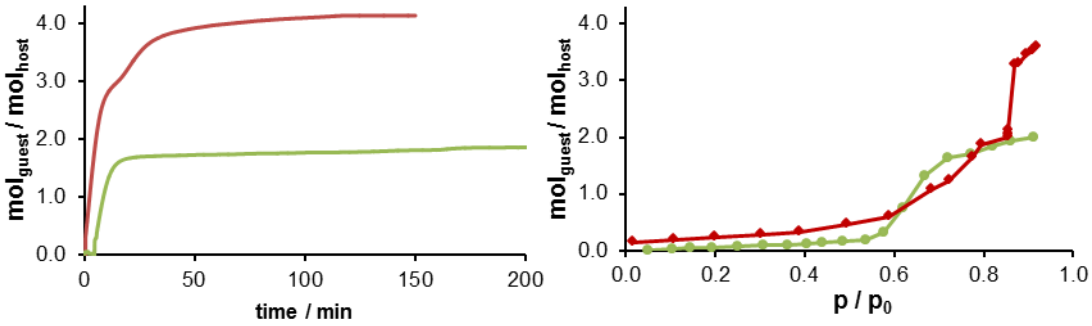

Figure 3: measurements of the solid-vapour reaction between **1** and benzene (red), and toluene (green) under kinetic (left) and thermodynamic (right) conditions.

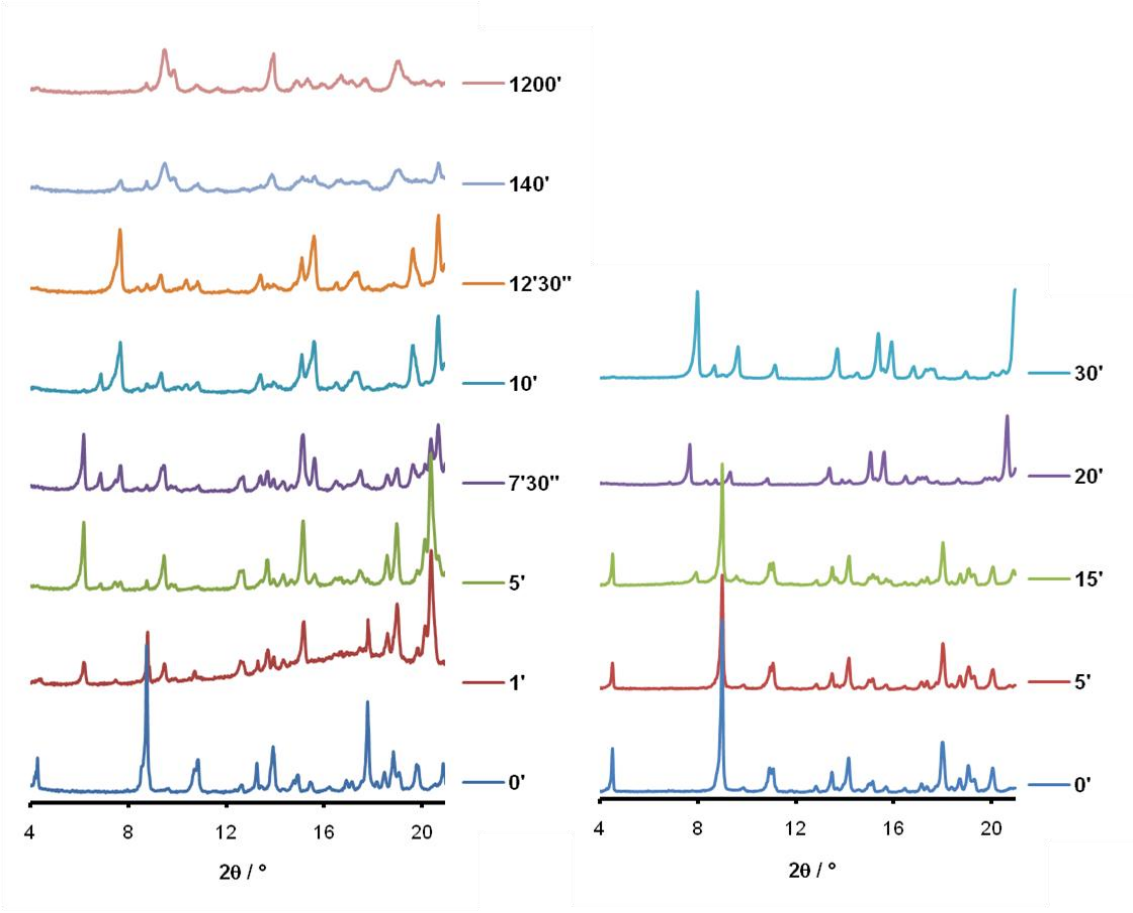

Figure 4: Time lapse PXRD of the solvent absorption (left) and vapour absorption (right) processes by **1**.

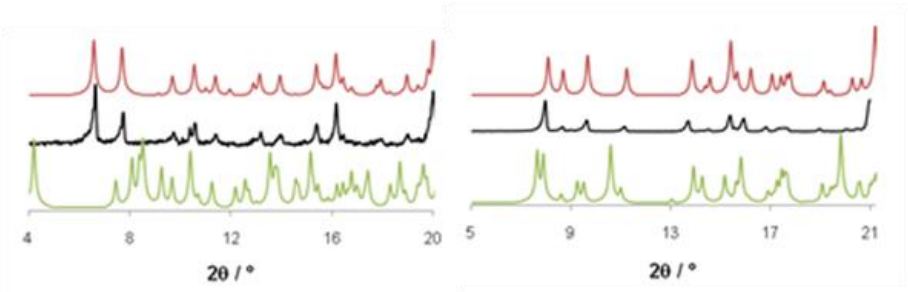

Figure S1: comparison of PXRD pattern. Left: calculated for **1** (green); measured for the product of the solid-vapour reaction with benzene (black); Calculated for **1bnz4** (red). Right: caclulated for **1tol II** (green); measured for the product of the solid-vapour reaction with toluene (black); caclulated for **1tol I** (red).