Supplementary Information

New Supramolecular Isomers with 2D 4^4 Square-Grid and 3D $6^5 \cdot 8$ Frameworks in One-Pot Synthesis; Reversible Solvent Uptake and Intriguing Luminescence Properties

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### [Ni(4-bpd)$_2$(NCS)$_2$]·3EtOH·H$_2$O (1) and [Ni(4-bpd)$_2$(NCS)$_2$]·EtOH·H$_2$O (2):

A solution (4 mL) of KSCN, 4.9 mg, 0.025 mmol) was added sol to a solution (8 mL) of NiCl$_2$·6H$_2$O (6.0 mg, 0.025 mmol) and 4-bpd (5.4 mg, 0.025 mmol) at room temperature. The resulting solution (pH = 6.47) was allowed to stand for several days to give purple crystals of **1** (7.5 mg) and light-yellow crystals of **2** (6.8 mg) in 40% and 32% yields, respectively. IR (KBr pellet) for **1**: ν = 3435 (m, sharp) 2070 (vs, sharp), 1611 (vs, sharp), 1553 (m, sharp), 1415 (m, sharp), 1311 (m, sharp), 1235 (m, sharp), 1061 (m, sharp), 1018 (m, sharp), 950 (w, sharp), 820 (m, sharp), 689 (m, sharp), 549 (m, sharp), 528 (m, sharp) cm^{-1}. Anal. Calc. for C$_{26}$H$_{20}$N$_{10}$NiS$_2$ (**1**) after desolvation (Mr = 594.34): C 52.45, N 23.54, H 3.22; Found: C 51.13, N 22.94, H 3.24. IR (KBr pellet) for **2**: ν = 3502 (s, sharp) 2073 (vs, sharp), 1610 (vs, sharp), 1558 (m, sharp), 1417 (m, sharp), 1310 (m, sharp), 1235 (m, sharp), 1061 (m, sharp), 1017 (m, sharp), 950 (m, sharp), 822 (m, sharp), 689 (m, sharp), 528 (m, sharp) cm^{-1}.Anal. Calc. for C$_{26}$H$_{20}$N$_{10}$NiS$_2$ (**2**) after desolvation (Mr = 594.34): C 52.45, N 23.54, H 3.22; Found: C 51.13, N 22.94, H 3.24.

Spectral measurement of [Ni(4-bpd)$_2$(NCS)$_2$]·3EtOH·H$_2$O (1) and [Ni(4-bpd)$_2$(NCS)$_2$]·2EtOH·2H$_2$O (2):

In order to investigate the possible differences in photoluminescence between (**1**) and (**2**) due to the variation of topologies, these complexes were measured with a confocal mode of a Witec-Alpha scanning near-field optical microscope (Ulm, Germany). A 406-nm laser line (GaN laser, Oxxius SN00223) was used as an excitation source throughout the measurement. The photoluminescence was separated from the scattering light of excitation pulse by a long-pass filter (LP02-442RU-25, Semrock) and sent by an optical fiber to the entrance slit of a polychromator (blazed at 520 nm) coupled by a sensitive charge coupled detector (CCD, Princeton Instruments, PI-MAX). The CCD was operated in shutter mode and the measurements were performed with 300 ms exposure time. All spectra were accumulated over an average 100 scans. The lifetime measurements were performed by using a mode-locked Ti:sapphire laser (Tsunami, Spectra-Physics) with an 80MHz repetition rate. This laser beam was directed into a doubling crystal (BBO) to yield an UV beam as a pulsed excitation source, then to a telescope for focusing. The confocal microscope (AlphaSNOM, WITec) was applied to monitor the crystals **1** and **2** respectively. The fluorescence signal from the crystals is analyzed by the time-correlated single photon counting system (SPC-300, Becker & Hickl) and high speed photodetector module (OT900, Edinburgh).
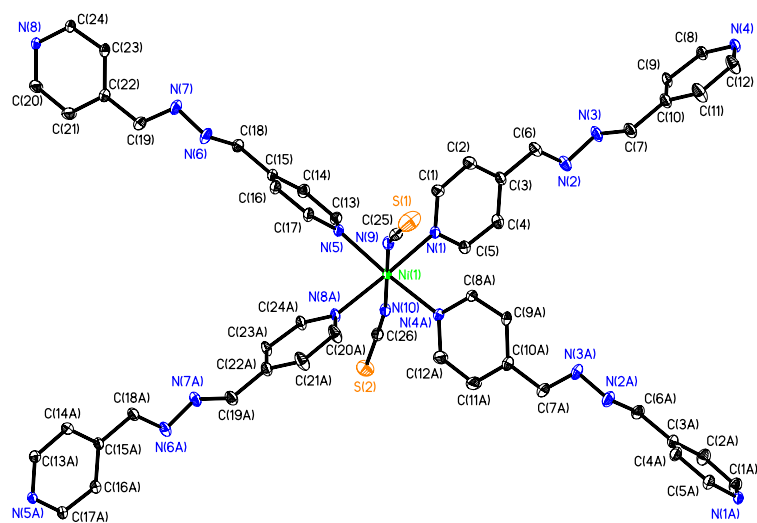
(a)
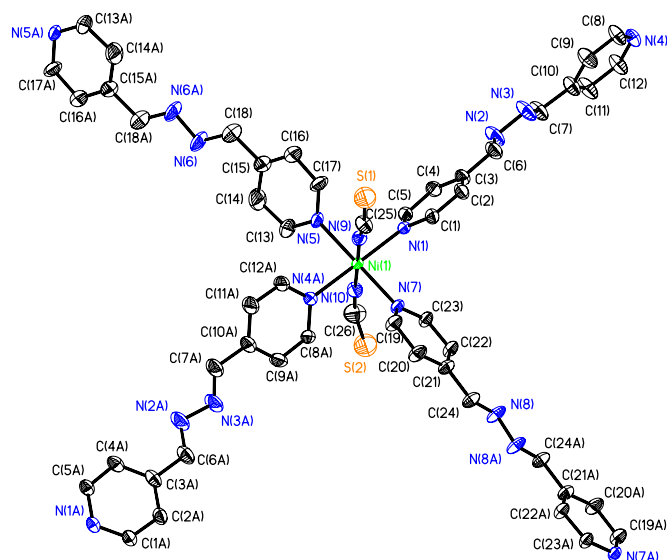
(b)

Figure S1. ORTEP views of pseudo "square-planar node" environment at the nickel(II) centers of (a) **1** and (b) **2**. Thermal ellipsoids are drawn at the 30% probability level. Bond lengths [Å]: Ni−N 2.054(4)−2.146(3) Å for **1** and Ni−N 2.034(6)−2.133(5) Å for **2**. The asymmetric unit in **2** has one 4-bpd ligand in a general position and two independent half 4-bpd ligands each lying about independent inversion centres. Symmetry transformation: (−x, −y−1, −z) for N(1A) to N(4A), C(1A) to C(12A) and (−x+2, −y−1, −z−1) for N(5A) to N(8A), C(13A) to C(24A) in **1**, and (x−1, −y+1/2, z−1/2) for N(1A) to N(4A), C(1A) to C(12A); (−x+1, y+3/2, −z+3/2) for N(5A), N(6A), C(13A) to C(18A); (−x, y+1/2, −z+5/2) for N(7A), N(8A) and C(19A) to C(24A) in **2**.
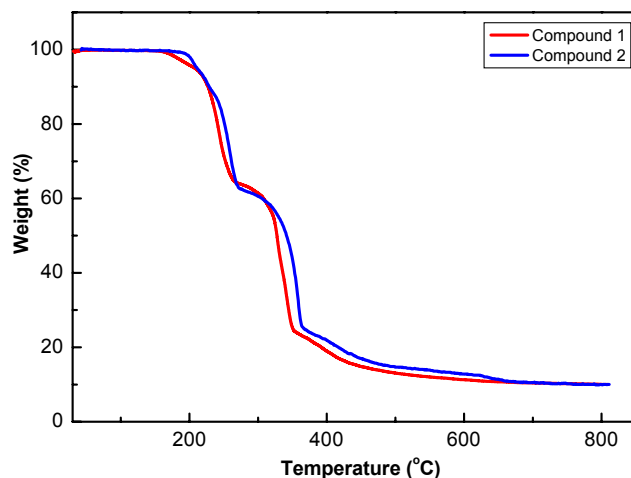
Figure S2. Thermogravimetric (TG) analysis of compounds **1** (red) and **2** (blue). Prior to the TGA measurements, both samples have been placed in the oven at 120 °C for de-solvation treatment.

Table S1. The O−H···O H-bonds for **1**^{a}

D−H···A (Å)	D−H (Å)	H···A (Å)	D···A (Å)	∠ D−H···A (°)
O(1)−H(1')···O(2)	0.90	1.88	2.771	170.6
O(1)−H(1)···O(3)$_i$	0.90	1.89	2.781	167.4
O(3)−H(3)···O(1)	0.84	1.89	2.711	167.2

^{a}Symmetry code: (i) = x, −y+3/2, z+1/2

Table S2. Dihedral angles of the R−C=N−N=−R units for **1** and **2**.^{a}

1	C(3)-C(6)-N(2)-N(3) 179.9	C(6)-N(2)-N(3)-C(7) 89.4	N(2)-N(3)-C(7)-C(10) 178.5
	C(15)-C(18)-N(6)-N(7) 178.1	C(18)-N(6)-N(7)-C(19) 105.4	N(6)-N(7)-C(19)-C(22) 176.7
2	C(3)-C(6)-N(2)-N(3) 179.1	C(6)-N(2)-N(3)-C(7) 148.0	N(2)-N(3)-C(7)-C(10) 179.6
	C(15)-C(18)-N(6)-N(6A) 179.5	C(18)-N(6)-N(6A)-C(18A) 180.0.0	
	C(21)-C(24)-N(8)-N(8B) 179.5	C(24)-N(8)-N(8B)-C(24B) 180.0.0	

^{a}Symmetry code: (A) = −x+1, y+3/2, −z+3/2; (B) = −x, y+1/2, −z+5/2