Electronic Supplementary Material (ESI) for CrystEngComm

Design of microporous mixed zinc-nickel triazolate metal-organic frameworks with functional ligands

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1. General considerations

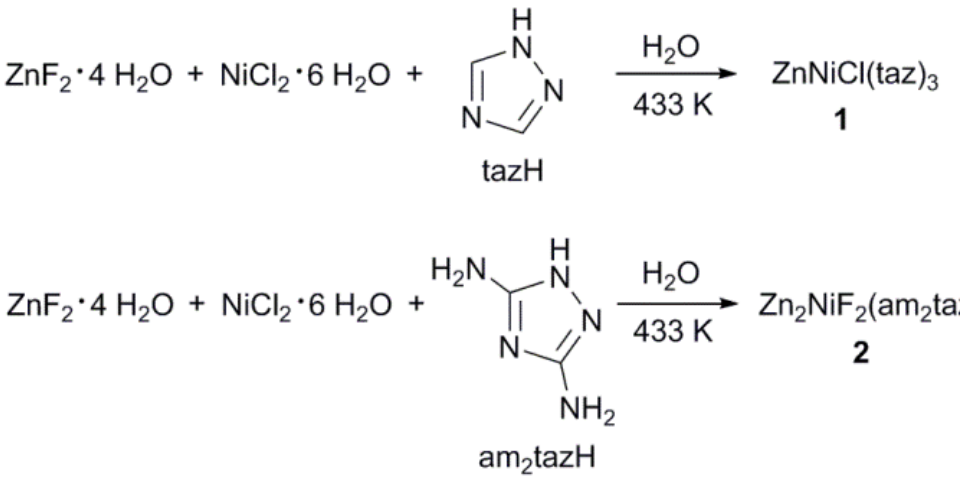
Chemicals

All chemicals were used as received without any further purification.

X-ray analysis

The X-ray powder diffraction (XRPD) diagram of $Zn_2NiF_2(am_2taz)_4$ (**2**) was collected at room temperature on a Bruker D8 ADVANCE diffractometer (Bragg–Brentano geometry, Cu Kα radiation, 50 kV, 35 mA, λ= 0.154184 nm). Measurements were done in the 4-90° 2θ range with a step of 0.02°. The synchrotron powder diffraction (SPD) diagram of $ZnNiCl(taz)_3$ (**1**) was collected at room temperature using the Crystal beamline at the synchrotron source SOLEIL, France. The wavelength was 0.7252 Å, and the diagram was collected in the 0-40° 2θ range. The sample was packed in a 0.8 mm diameter capillary and spun at 10 Hz. Total collection time was 45 minutes.

2. Synthesis



In a typical synthesis, zinc fluoride tetrahydrate (0.526 g, 3 mmol) and nickel dichloride hexahydrate (0.71 g, 3 mmol) are allowed to react in a 50 mL Teflon-lined stainless steel autoclave with 1,2,4-triazole (0.42 g, 6 mmol) in 30 mL of water at 433 K for four days to give

$ZnNiCl(taz)_3$ (**1**) as a violet powder after washings with water and ethanol and drying under air at 363 K.

Similarly, $Zn_2NiF_2(am_2taz)_4$ (**2**) is prepared usingthe same chemicals except that the 1,2,4-triazole is replaced by the 3,5-diamino-1,2,4-triazole (0.6 g, 6 mmol) as organic ligand. $Zn_2NiF_2(am_2taz)_4$ (**2**) is obtained as a pale green solid after whasings with water and ethanol and drying at 363 K.

Table S1. Elemental Analyses

Sample	**Zn**	**Ni**	**Cu**	**Cl**	**F**	**C**	**N**
	%	%	%	%	%	%	%
$ZnNiCl(taz)_3$ (**1**)	18.02	15.78		8.26	< 0.2	20.08	33.83
	18.91	16.52				19.75	33.22
$Zn_2NiF_2(am_2taz)_4$ (**2**)	24.61	7.33		< 0.20	5.88	9.52	43.78
	24.50	7.24					43.37

3. Structure refinement

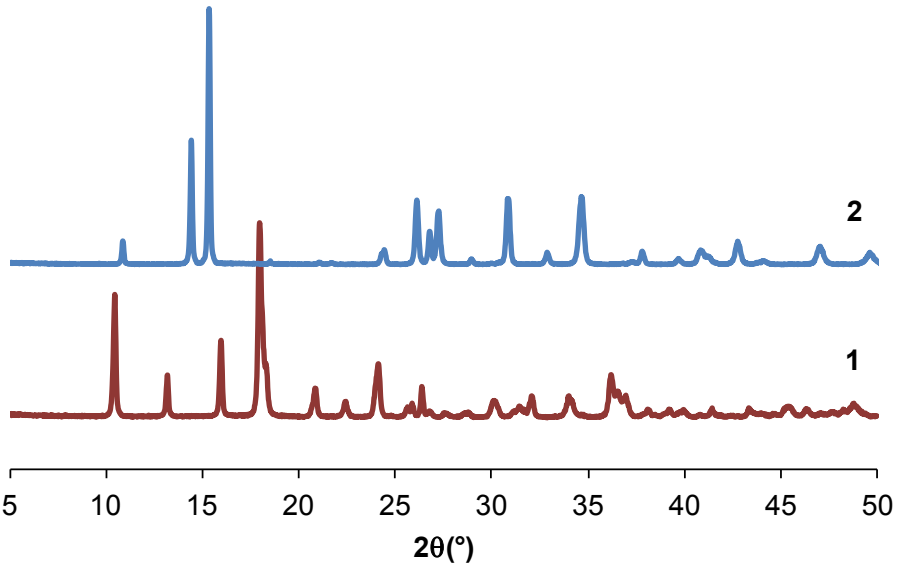


Fig. S1 PXRD patterns of $ZnNiCl(taz)_3$ (**1**) and $Zn_2NiF_2(am_2taz)_4$ (**2**).

(a) (b)

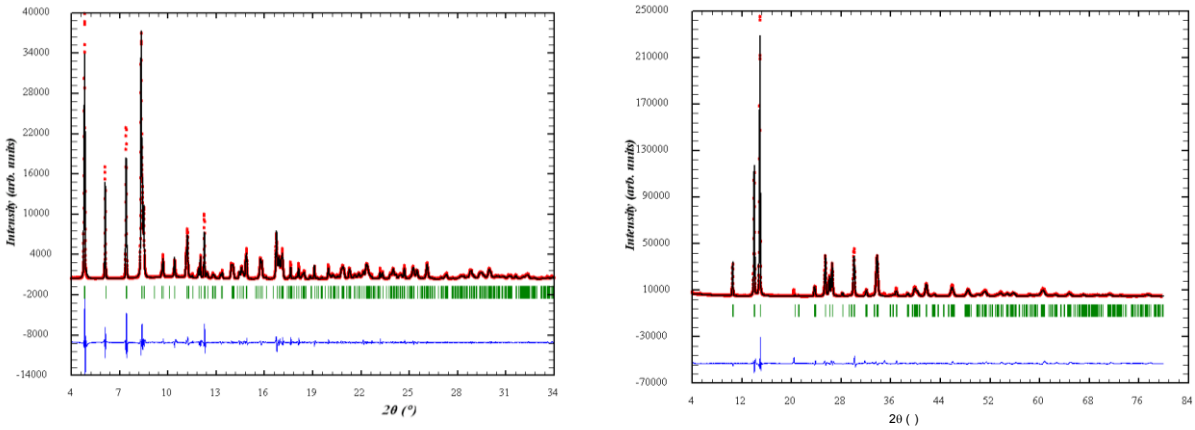


Fig. S2 Experimental (red) and calculated (black) (a) SPD patterns of $ZnNiCl(taz)_3$ (**1**) and (b) XRPD patterns of $Zn_2NiF_2(am_2taz)_4$ (**2**) resulting from the Rietveld refinement. The difference between calculated and experimental patterns (blue) and the Bragg positions (green) are given below. R_p = 0.130, R_{wp} = 0.153, R_{Bragg} = 0.064 for (a) and R_p = 0.100, R_{wp} = 0.113, R_{Bragg} = 0.054 for (b). Exchanging the cation positions yields similar R_{Bragg} values.

Table S2 Crystal data and structure refinement of $Zn_2NiF_2(am_2taz)_4$ (**2**) and $ZnNiCl(taz)_3$ (**1**).

Compound	$ZnNiCl(taz)_3$ (**1**)	$Zn_2NiF_2(am_2taz)_4$ (**2**)
Empirical Formula	$C_6N_9ClZnNi$	$C_8H_{16}F_2N_{20}Zn_2Ni$
Crystal system	Orthorhombic	tetragonal
Space group	Pnma (62)	P4/nnc (126)
a (Å)	7.383 (1)	11.877(1)
b (Å)	9.870(1)	11.877(1)
c (Å)	17.293(1)	7.469(2)
V ($Å^3$), Z	1260.1(1), 4	1053.6(1), 2
Wavelength (Å)	0.7252	1.54056
2θ range (°)	0-40	4-90

Table S3 Atom, Wyckoff multiplicity, site symmetry, atomic coordinates and isotropic displacement parameters U_{iso} ($Å^2$) determined from the Rietveld refinement of the SPD pattern of $Zn_2NiF_2[am_2taz]_4$. Uncertainties are given in brackets.

Atom Label	Site	x	y	z	U_{iso}
Ni1	2*b*	0.25	0.25	0.75	0.00496(2)
F1	4*e*	0.25	0.25	0.0364(1)	0.01540(3)
N1	8*j*	0.75	0.563(1)	0.25	0.00407(2)
C2	16*k*	0.2115(1)	0.4936(1)	0.6073(1)	0.00987(2)
N2	16*k*	0.7251(1)	0.3865(1)	0.1633(1)	0.00407(2)
N3	16*k*	0.4676(1)	0.3354(1)	0.4422(1)	0.00407(2)
Zn1	4*d*	0.75	0.25	0.5	0.01114(2)

Table S4 Atom, Wyckoff multiplicity, site symmetry, atomic coordinates and isotropic displacement parameters B_{iso} ($Å^2$) determined from the Rietveld refinement of the XRPD pattern of $ZnNiCl(taz)_3$. Uncertainties are given in brackets.

Atom Label	Site	x	y	z	B_{iso}
Ni1	4*c*	-0.1259(2)	0.75	0.4215(4)	1.2(1)
Zn1	4*c*	-0.4760(7)	0.25	0.2607(2)	2.3(1)
Cl1	4*c*	0.1857(8)	0.75	0.4259(6)	3.2(2)
N1	8*d*	-0.3063(2)	0.0968(1)	0.3089(1)	2.2(2)
N2	8*d*	-0.1354(2)	0.0823(1)	0.3015(1)	2.2(2)
N3	8*d*	-0.1934(2)	0.9073(1)	0.3674(1)	2.2(2)
N4	4*c*	-0.2115(3)	0.75	0.5317(1)	2.2(2)
N5	4*c*	-0.1710(3)	0.75	0.6556(1)	2.2(2)
N6	4*c*	-0.3518(3)	0.75	0.6382(1)	2.2(2)
C1	8*d*	-0.3449(3)	0.9935(2)	0.3517(1)	1.4(3)
C2	8*d*	-0.0596(3)	0.9815(2)	0.3302(1)	1.4(3)
C3	4*c*	-0.3915(3)	0.75	0.5585(1)	1.4(3)
C4	4*c*	-0.0740(3)	0.75	0.5817(1)	1.4(3)

4. Gas sorption

The N_2 adsorption/desorption isotherms at 77 K were measured on a BELSORP-Mini. The samples were outgassed under vacuum (~ 10^{-4} mbar) at 393 K for 12 h before start of the measurements. The specific surface was determined by BET method.

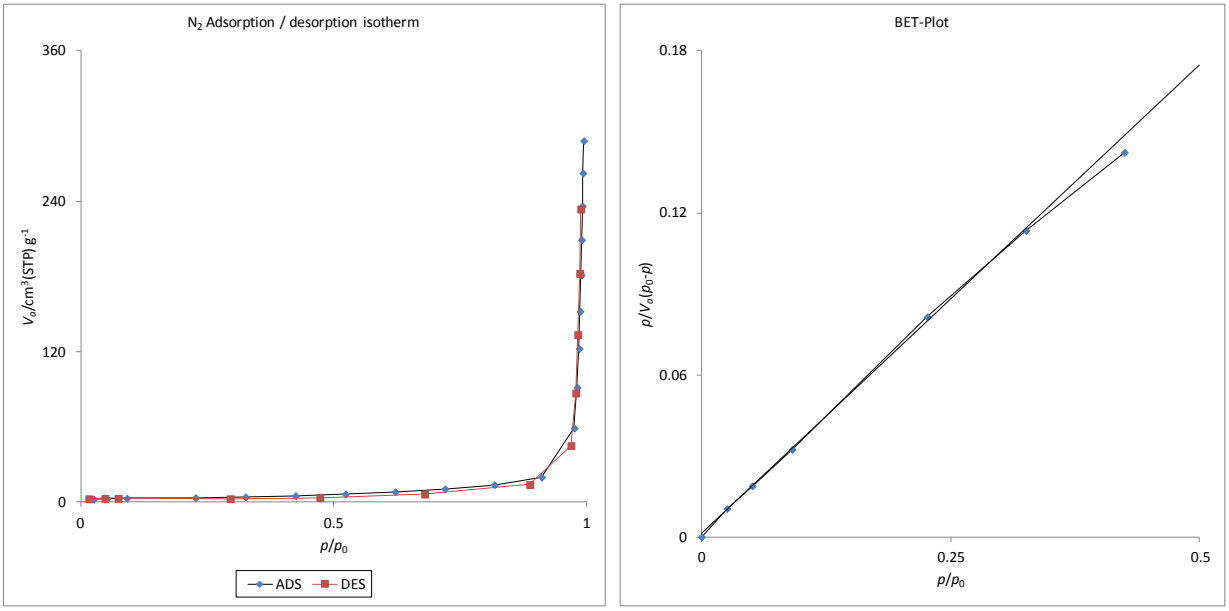


Fig. S3 N_2 adsorption isotherm of $ZnNiCl(taz)_3$ (**1**) (left) and BET plot (right, $a_{s,BET}$ = 12.5 $m^2.g^{-1}$, C = 238).

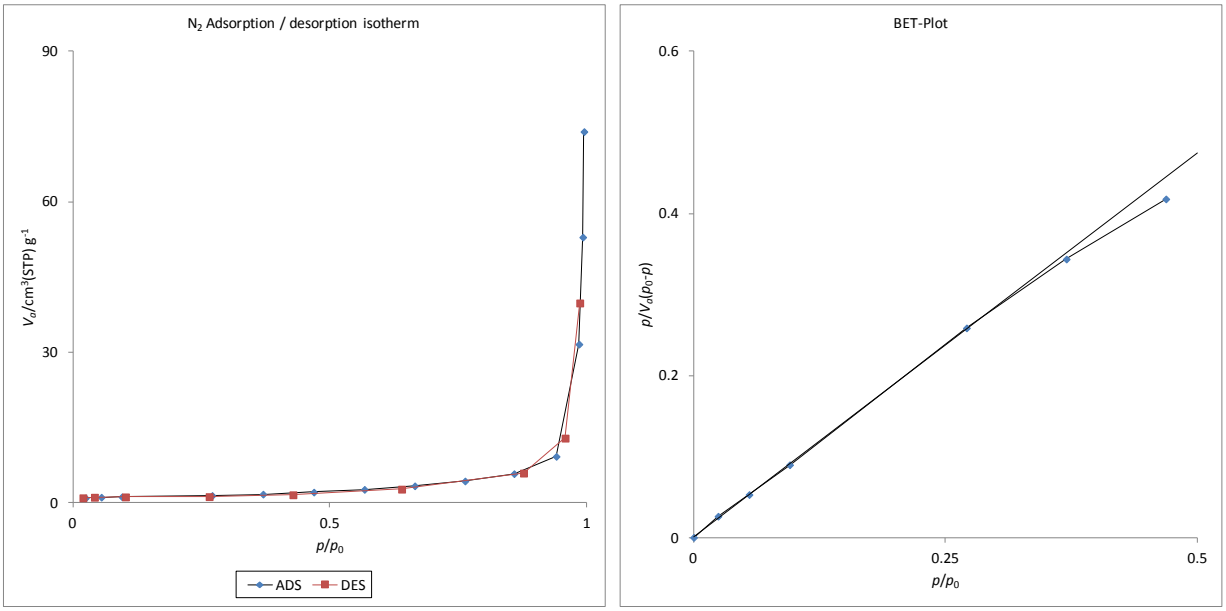


Fig. S4 N_2 adsorption isotherm of $Zn_2NiF_2(am_2taz)_4$ (**2**) (left) and BET plot (right, $a_{s,BET}$ = 4.6 $m^2.g^{-1}$, C = 742).

The CO_2 adsorption/desorption isotherms at 303 K were measured on a BELSORP-HP. The sample was outgassed under vacuum (~ 10^{-4} mbar) at 473K for 12 h before start of the measurements.

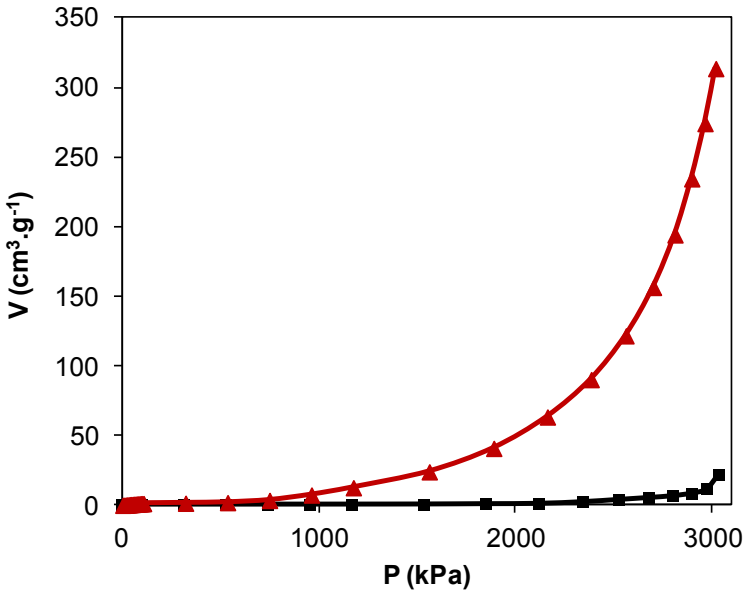


Fig. S5 CO_2 adsorption isotherms of **1** (■) and **2** (▲) performed at 303 K.

5. Photoluminescence

Photoluminescent (PL) measurements were carried out with the use of laser diode with the excitation photon energy at 3.62 eV (343 nm). The laser spot area was about 10^{-4} cm^{-2}. The spectral decomposition of the PL signal was performed by Horiba JobinYvon iHR-320 monochromator. The PL spectra were detected by nitrogen-cooled CCD camera Horiba Symphony 1024x256. All spectra were corrected using the spectral response function of whole PL system.

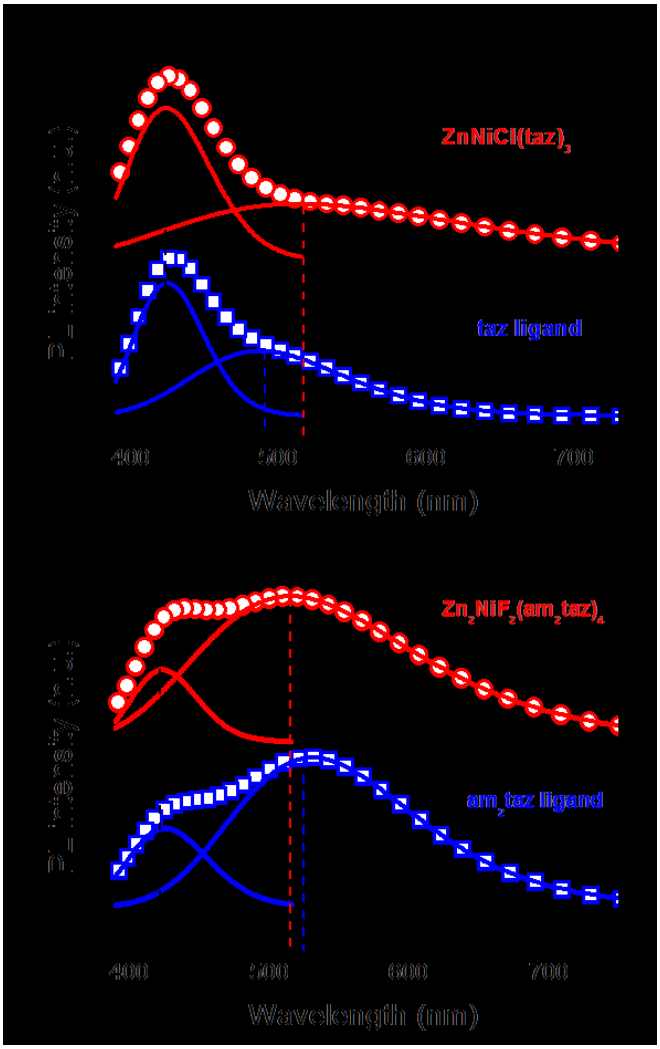


Fig. S6 Room temperature visible photoluminescence spectra of A) $ZnNiCl(taz)_3$, **1** (circles) and its parent ligand Htaz (squares) and B) $Zn_2NiF_2(amtaz)_4$, **2** (circles) and parent ligand Ham_2taz (squares). Excitation wavelength: 343 nm.