Electronic Supplementary Material (ESI) for CrystEngComm.

Supplementary Information for the Manuscript

Nickel(II) and Copper(I,II)-Based Metal-Organic Frameworks Incorporating an Extended Tris-pyrazolate Linker

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S.1. Synthesis of 1,3,5-tris-*p*-(1*H*-pyrazol-4-yl)phenyl)benzene (H_3BTPP)

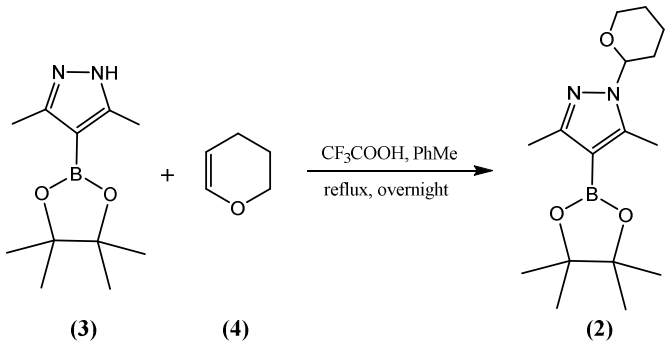
S.1.1. Synthesis of 1,3,5-tris(4-bromophenyl)benzene (1). **1** was prepared from 4-bromoacetophenone following the procedure already reported in literature.[1] When necessary, recrystallization of **1** was carried out in boiling toluene, affording light yellow needles (yield: 80%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.73 (s, 3H), 7.66-7.64 (d, 6H), 7.59-7.57 (d, 6H). IR (cm^{-1}): 3030 (vw), 1594 (m), 1487 (s), 1378 (m), 1244 (w), 1073 (s), 1005 (s), 804 (vs).

S.1.2. Synthesis of 1-(tetrahydro-pyran-2-yl)-4-pyrazoleboronic acid pinacol ester (2). **2** was prepared by protecting 4-pyrazoleboronic acid pinacol ester (**3**) with 3,4-dihydro-2*H*-pyran (**4**), following a modified procedure (Scheme S1) with respect to the one already proposed in the literature[2]. A solution of **3** (2.44 g, 0.01 mol), **4** (1.57 g, 1.71 mL, 0.02 mol) and trifluoroacetic acid (0.56 mL, 0.32 mmol) in toluene (100 mL) was stirred at reflux for 24 h. After cooling down to room temperature, the solvent was evaporated with a rotary evaporator and the light brown oil was passed through a chromatographic column, using ethyl acetate:hexane (3.5:1) as eluent. After the evaporation of the solvents by rotavapor, a yellowish oil was obtained which was left under vacuum till **2** precipitated in the form of a white solid (yield: 76%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.95 (s, 1H), 7.86 (s, 1H), 5.44 (t, 1H), 4.06-3.68 (m, 2H), 2.09-2.05 (m, 2H), 1.70-1.61 (m, 4H), 1.31 (s, 12H). IR (neat, cm^{-1}): 3103 (w), 2975 (m), 2957 (m), 2929 (m), 2846 (w), 1559 (vs), 1441 (w), 1390 (m), 1259 (s), 1140 (s), 1080 (s), 908 (m), 852 (s), 696 (s).

S.1.3. Synthesis of 1,3,5-tris-*p*-(1*H*-pyrazol-4-yl)phenyl)benzene (H_3BTPP). **H_3BTPP** was synthesized according to Scheme S2 by performing a Suzuki coupling reaction between 1,3,5-tris(4-bromophenyl)benzene (**1**) and 1-(tetrahydro-pyran-2-yl)-4-pyrazoleboronic acid pinacol ester (**2**), yielding 1,3,5-tri-*p*-((1-(tetrahydro-pyran-2-yl)-pyrazol-4-yl)phenylbenzene (**5**), following a slightly adapted procedure with respect to the one reported previously.[3] A mixture of dioxane/water (100 mL, 1:1 v/v) containing **1** (1.08 g, 1.99 mmol), **2** (1.80 g, 6.47 mmol), tetrakis(triphenylphosphine)palladium (0.23 g, 0.20 mmol), potassium carbonate (3.25 g, 0.024 mol) and lithium chloride (0.14 g, 0.003 mol), was heated at 75-80 °C under stirring for 72 h. The

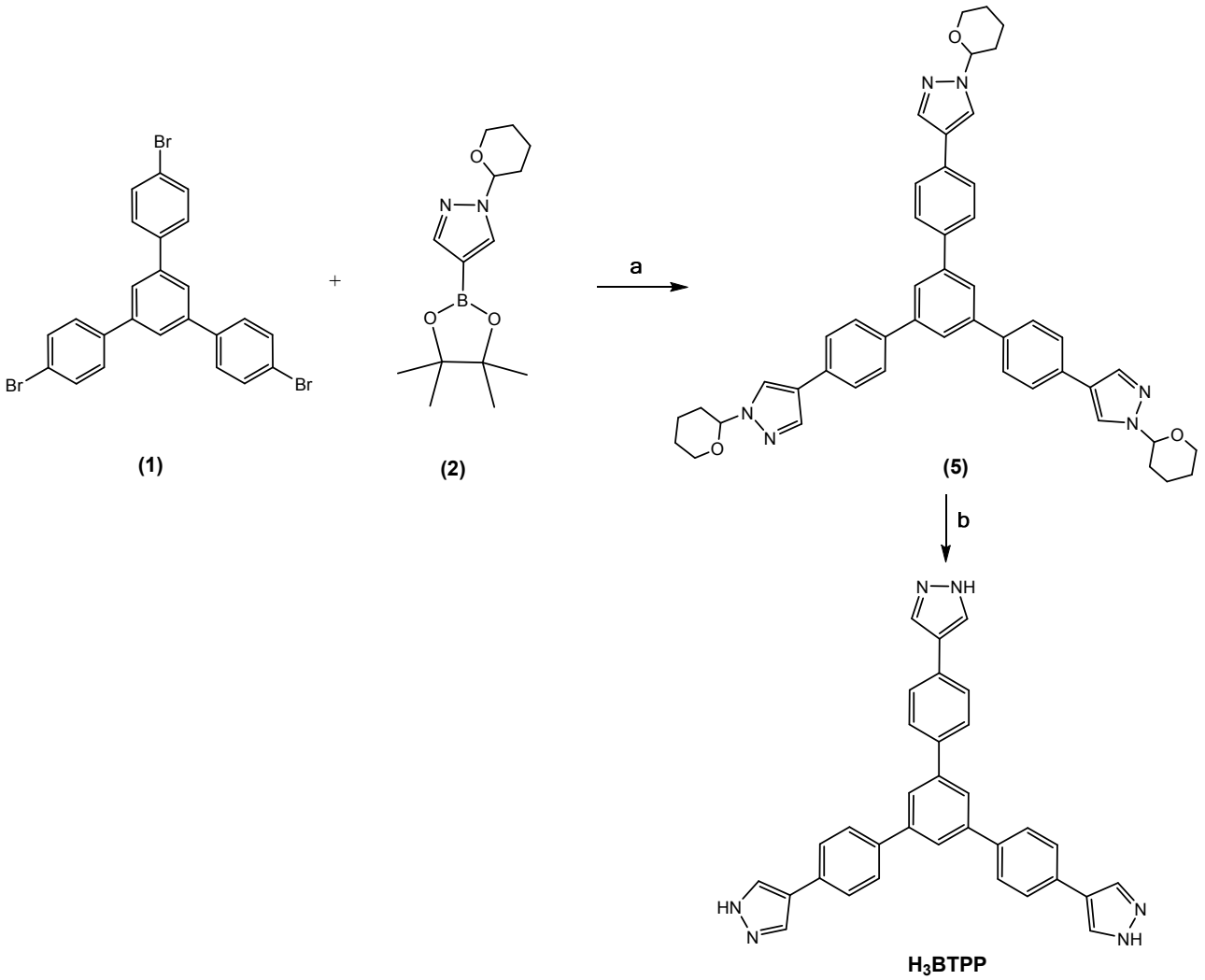
resulting white precipitate was filtered off, dried under vacuum and then purified by column chromatography using ethyl acetate/hexane (15:1) as eluent. (yield: 75%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 7.94-7.90 (d, 6H), 7.81 (s, 3H), 7.73-7.71 (d, 6H), 7.63-7.61 (d, 6H), 5.46-5.43 (m, 3H), 4.24-3.71 (m, 6H), 2.18-2.15 (m, 6H), 1.66-1.25 (m, 6H), 0.92-0.90 (m, 6H). IR (neat, cm^{-1}): 3103 (w), 3030 (w), 2946 (m), 2849 (w), 1612 (w), 1595 (w), 1572 (m), 1507 (w), 1432 (m), 1375 (m), 1183 (m), 1080 (s), 1039 (s), 977 (s), 952 (s), 910 (s), 825 (s), 542 (m).

Finally, 1,3,5-tri-*p*-(1*H*-pyrazol-4-yl)phenylbenzene (**H_3BTPP**), was obtained by deprotecting **5** in ethanol (100 mL) in the presence of 1 M HCl (10 mL) under reflux for 12 h. The product precipitated as a yellowish solid which was filtered off, dried under vacuum and purified by recrystallization from boiling dimethylformamide/methanol (1:1, v/v) (yield: 72%). **H_3BTPP** is soluble in methanol, dimethylformamide and dimethylsulfoxide. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ: 8.15 (s, 6H), 7.87-7.84 (m, 9H), 7.74-7.71 (d, 6H). ESI-MS (+) MeOH *m/z* 504 (100%). IR (neat, cm^{-1}): 3169 (br), 2949 (br), 1610 (w), 1593 (w), 1574 (m), 1509 (m), 1371 (m), 1142 (m), 1030 (s), 946 (vs), 815 (vs), 675 (m), 531 (m). Elem. Anal. Calcd. for $C_{33}H_{24}N_6$ (FW = 504.59 g/mol): C, 73.32; H, 5.22; N, 15.55%. Found: C, 73.64; H, 5.12; N, 15.05%.



(3) (4) (2)

Scheme S1. Schematic representation of the synthetic route to 1-(tetrahydro-pyran-2-yl)-4-pyrazoleboronic acid pinacol ester (**2**).



(1) (2) (5) H_3BTPP

Scheme S2. Schematic representation of the synthetic route to **H_3BTPP**: a) $Pd(PPh_3)_4$, K_2CO_3, LiCl, Dioxane/H_2O, 75-80 °C, 72 h; b) 1 M HCl, EtOH, reflux 12 h.

S.2. X-ray crystallography

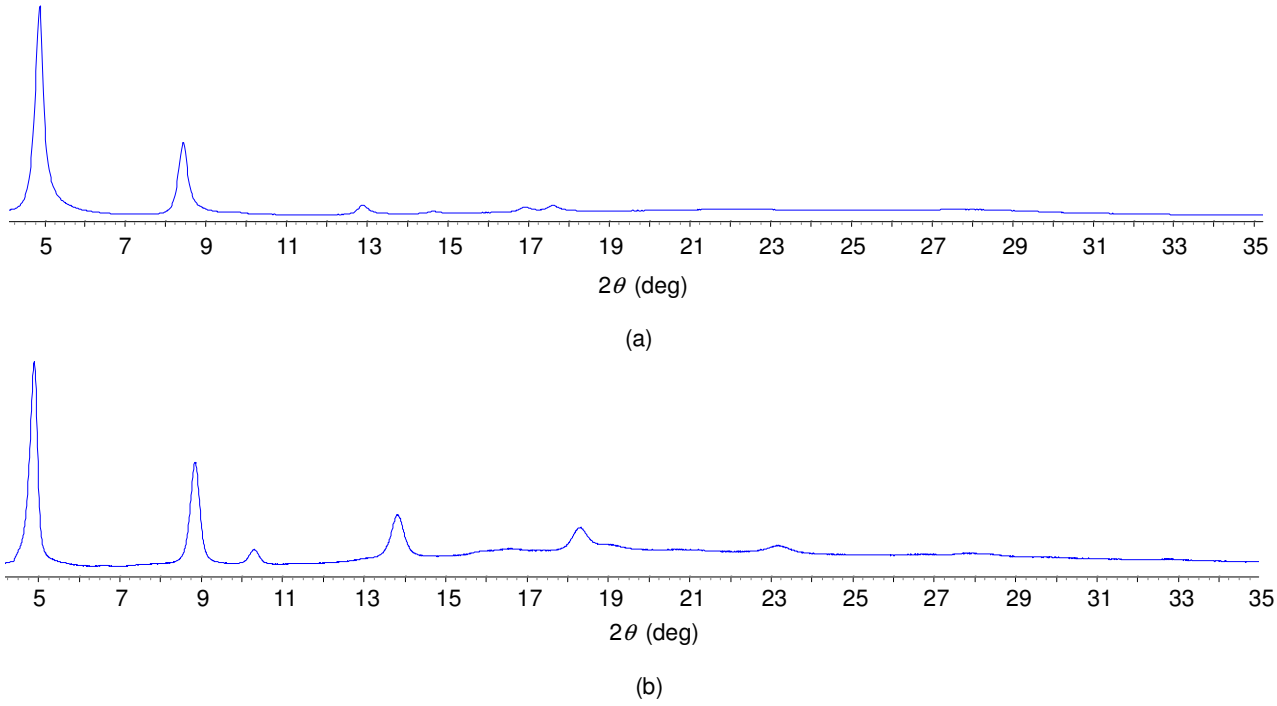


Figure S1. Small-to-medium 2θ angle portion of the X-ray powder diffraction figures of as-synthesized (a) **Cu-BTPP** and (b) **Ni-BTPP**, denouncing the very low degree of crystallinity of the two MOFs.

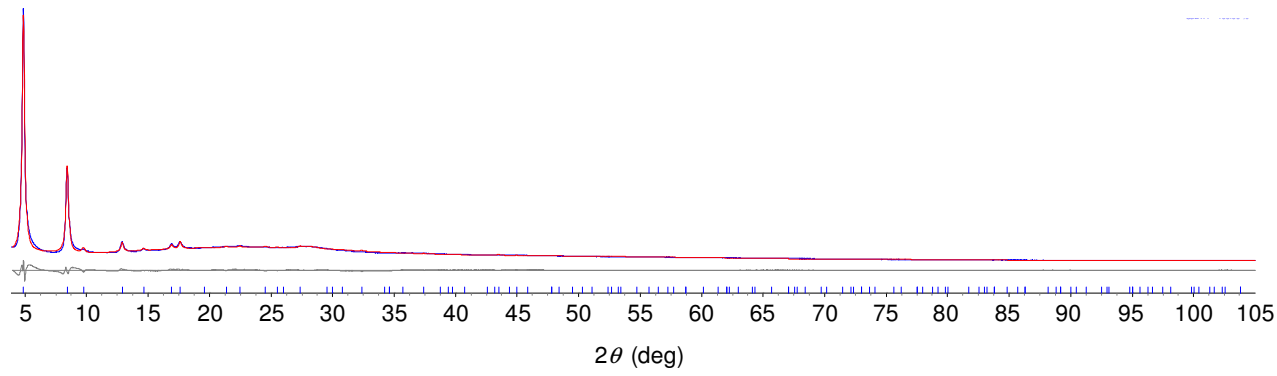


Figure S2. Graphical results of the Rietveld refinement carried out **Cu-BTPP** by adopting a 2-D structural model (see the main text for further details), in terms of experimental, calculated and difference traces (blue, red and gray, respectively). The markers of the Bragg peaks are reported at the bottom. Horizontal axis, 2θ (deg); vertical axis, intensity (counts).

S.3. Infrared spectroscopy

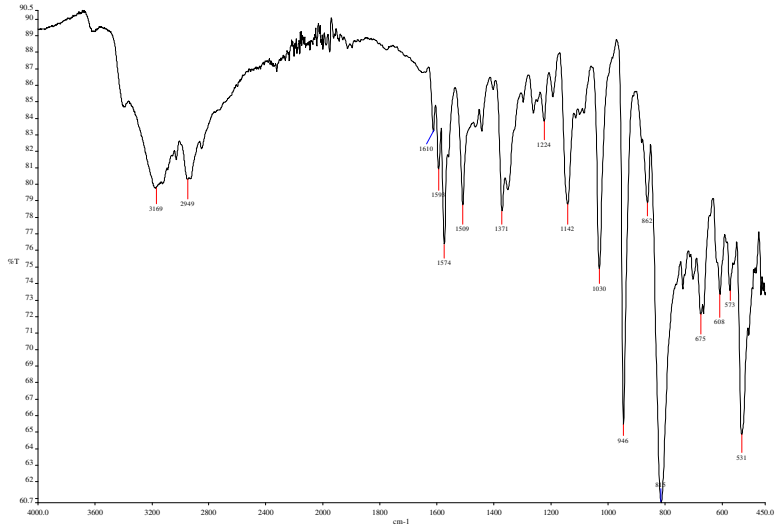


Figure S3. Infrared spectrum of **H_3BTPP**.

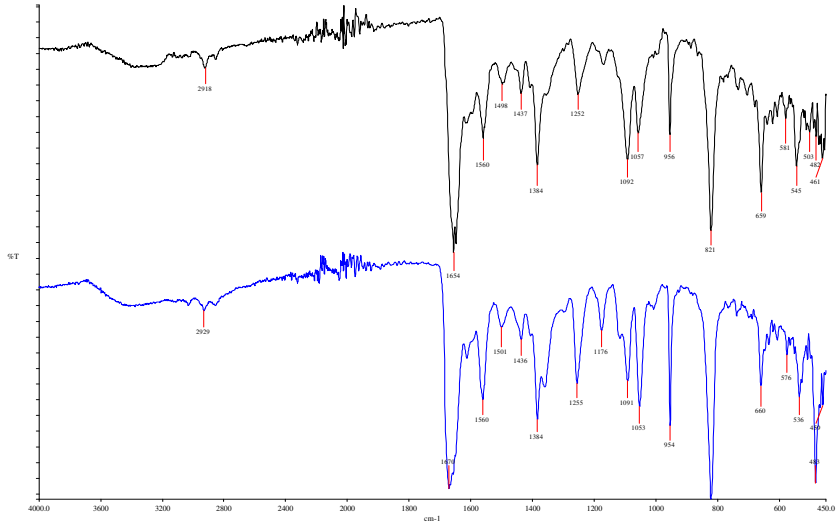


Figure S4. Infrared spectra of as-synthesized **Cu-BTPP** (blue) and **Ni-BTPP** (black).

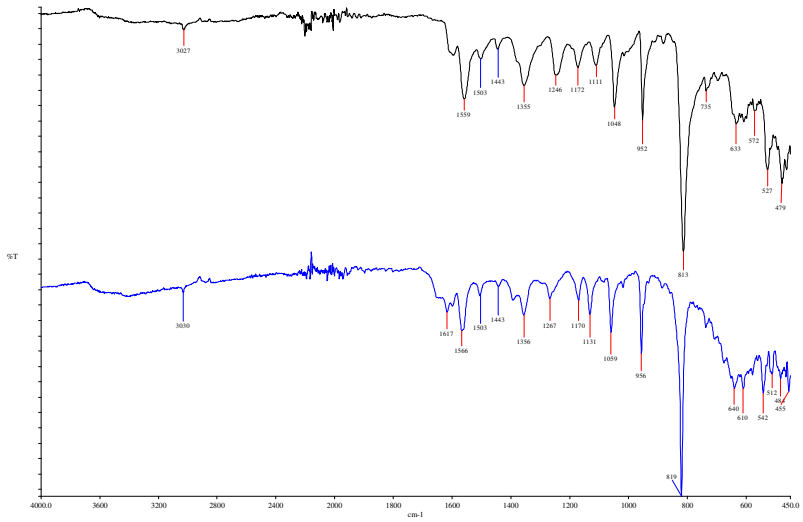


Figure S5. Infrared spectra of **Cu-BTPP** evacuated at 200 °C (black) and of **Ni-BTPP** evacuated at 250 °C (blue).

S.4. Adsorption measurements

Table S1. BET fitting parameters from the N_2 adsorption isotherms for **Cu-BTPP** and **Ni-BTPP**.

Fitting parameters	**Cu-BTPP**	**Ni-BTPP**
Slope	0.006587226	0.002657377
Y-int	0.000003603	0.000002923
C	1829.358779	910.1268112
V_m (cm^3/g)	151.725997	375.8974633
R^2	0.999935914	0.999595503
P/P_0 Low	0.0243	0.016
P/P_0 High	0.0855	0.0666

REFERENCES

[1] Hu, H.; Zhang, A.; Ding, L.; Lei, X.; Zhang, L. *J. Chem. Res.* **2007**, *12*, 720-721.

[2] Mogi, M.; Kawanami, T.; Yamada, K.; Yasoshima, K.; Imase, H.; Miyake, T.; Ohmori, O. WO 2009071509, **2009**, Novartis AG, Switzerland.

[3] Angbrant, J.; Homan, E.; Lundbaek, T.; Martinsson, J.; Sari, M.; Joensson, M.; Faernegaardh, K.; Hallberg, K. WO 2011161201, **2011**, Kancera AB, Sweden.