Supporting Information for

When long bis(pyrazolates) meet late transition metals: structure, stability and adsorption of MOFs featuring large parallel channels

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Figure S1. Final Rietveld refinement plots for a) [Ni(BPEB)], b) α -[Zn(BPEB)], and c) [Fe₂(BPEB)₃], in terms of experimental (blue), calculated (red) and difference (grey) patterns. The positions of the Bragg reflections are indicated with blue marks at the bottom. The high-angle portion of the diffractograms has been magnified (4×) for the sake of clarity. Horizontal axis: 20, deg; vertical axis: intensity, counts.



Figure S2. Low-angle portion of the XRPD patterns acquired on different preparations of α -[Zn(BPEB)] and β -[Zn(BPEB)]. The difference between a prototypical pattern of the former (black curve) and one of the latter (orange curve), in terms of relative intensities of the peaks, is evident, above all for the first two Bragg reflections, for which the ratio of the peak intensities is reported on the right.



Figure S3. a) Electronic density map produced with the structure factors *observed* for β -[**Zn(BPEB)**]. b) Electronic density map produced with the structure factors *calculated* with the doubly interpenetrated network found in α -[**Zn(BPEB**)]. By comparing the two maps, it is evident that the doubly interpenetrated network describes only a part of the observed electronic density, that in the channels remaining at present unexplained, but possibly attributable to another [Zn(BPEB)] network incommensurate with the "major" one.



Figure S4. Traces of the thermogravimetric analyses (green) and the differential scanning calorimetry (blue) carried out for a) [Ni(BPEB)], b) [Fe₂(BPEB)₃], c) α -[Zn(BPEB)], and d) β -[Zn(BPEB)] in a flux of nitrogen at a rate of 10 °C/min.



Figure S5. a) Plot of the X-ray powder diffraction patterns measured on [**Ni(BPEB**)] as a function of the temperature heating, with steps of 20 °C, up to decomposition. The permanent porosity of species [**Ni(BPEB**)] can be appreciated. b) Percentage variation of the unit cell parameters (p_T) of [**Ni(BPEB**)] as a function of the temperature. The values at 30 °C (p_{30}) have been taken as the references. **a**, blue rhombi; **b**, red triangles; **c**, green circles; **V**, orange squares. c) Plot of the X-ray powder diffraction patterns measured on [**Ni(BPEB**)] during heating-cooling cycles within the range 50-210 °C. Heating step, red; cooling step, blue.



Figure S6. a) Plot of the X-ray powder diffraction patterns measured on α -[Zn(BPEB)] as a function of the temperature heating, with steps of 20 °C, up to decomposition. The permanent porosity of species α -[Zn(BPEB)] can be appreciated. b) Percentage variation of the unit cell parameters (p_T) of α -[Zn(BPEB)] as a function of the temperature. The values at 30 °C (p₃₀) have been taken as the references. **a**, blue rhombi; **b**, red triangles; **c**, green circles; **V**, orange squares. c) Plot of the X-ray powder diffraction patterns measured on α -[Zn(BPEB)] during heating-cooling cycles within the range 50-210 °C. Heating step, red; cooling step, blue.



Figure S7. Schematic representation of the chemical transformation from two acetylenic groups toward a tetrahedrane moiety.



Figure S8. a) Plot of the X-ray powder diffraction patterns measured on β -[Zn(BPEB)] as a function of the temperature heating, with steps of 20 °C, up to decomposition. The phase transformation from β -[Zn(BPEB)] to γ -[Zn(BPEB)] can be appreciated from about 210 °C. b) Percentage variation of the unit cell parameters (p_T) of α -[Zn(BPEB)] as a function of the temperature. The values at 30 °C (p₃₀) have been taken as the references. **a**, blue rhombi; **b**, red triangles; **c**, green circles; **V**, orange squares.



Figure S9. Chemical stability of $[Fe_2(BPEB)_3]$ upon exposure to water vapours at r.t., boiling water, aqueous acidic (pH 6) or basic (pH 8) solutions at r.t. The peak indicated with a blue asterisk in the pattern of the sample suspended in boiling water is the most intense Bragg reflection of the H₂BPEB ligand, witnessing progressive hydrolysis of the PCP during this harsh chemical treatment.



Figure S10. a) Chemical stability of α -[**Zn**(**BPEB**)] upon exposure to water vapours at r.t., boiling water, aqueous acidic (pH 6) or basic (pH 8) solutions at r.t. In all of the cases, appearance of the β phase is observed, as highlighted in b), where the progressive phase transition from α -[**Zn**(**BPEB**)] to β -[**Zn**(**BPEB**)] after 1, 5 and 8 hours in boiling water can be appreciated.



Figure S11. IAST selectivities of CO₂ over N₂ for 15:85 molar mixtures as determined from adsorption isotherms at 298 and 273 K on $[Fe_2(BPEB)_3]$ (dark grey), α -[Zn(BPEB)] (light grey) and [Ni(BPEB)] (orange).



Figure S12. Isoteric heat of adsorption for CO_2 of [Fe₂(BPEB)₃] (dark grey), α -[Zn(BPEB)] (light grey) and [Ni(BPEB)] (orange) using the Clausius-Clapeyron equation.



Figure S13. N₂ adsorption isotherms of $[Fe_2(BPEB)_3]$ after the first activation treatment at 120 °C under vacuum (blue diamonds) and after several activation/gas-adsorption cycles (blue circles).



Figure S14. N₂ adsorption isotherms of $[Fe_2(BPEB)_3]$ and α -[Zn(BPEB)] after several activation/gas-adsorption cycles.



Figure S15. Fluorescence decay distribution obtained for the H₂BPEB ligand (red dots, all panels) compared with that observed for α -[Zn(BPEB)] (panel a, blue squares), [Fe₂(BPEB)₃] (panel b, cyan stars), and [Ni(BPEB)] (panel c, magenta crosses). The corresponding best-fitting curves are represented as solid lines of the same colors.

| | Т | Р | V _{ads} | m _{ads} | %wt | V/V | Qst |
|--|-----|----------------|-------------------------|------------------|------|-------|--------|
| | K | bar | cm ³ (STP)/g | mmol/g | | | kJ/mol |
| [Fe ₂ (BPEB) ₃] | 298 | 10 | 85.32 | 3.6 | 5.7 | 58.9 | 17 |
| | 273 | 10 | 114.6 | 5.1 | 8.2 | 79.0 | |
| | 195 | 1 ^a | 170.0 | 7.6 | 12.1 | 117.3 | |
| [Ni(BPEB)] | 298 | 10 | 38.9 | 1.6 | 2.6 | 20.6 | 18 |
| | 273 | 10 | 62.2 | 2.8 | 4.4 | 33.0 | |
| | 195 | 1 ^a | 62.3 | 2.8 | 4.4 | 33.0 | |
| α- [Zn(BPEB)] | 298 | 10 | 30.1 | 1.3 | 2.0 | 26.2 | 19 |
| | 273 | 10 | 71.5 | 3.2 | 5.1 | 62.2 | |
| | 195 | 1 ^a | 68.9 | 3.1 | 5.0 | 59.9 | |

Table S1. CH₄ adsorption capacities of [Fe₂(BPEB)₃], [Ni(BPEB)] and α -[Zn(BPEB)] at 298 K, 273 K and 195 K.

^a P/P₀ is reported.

Table S2. Fitting parameters for fluorescence decay time distributions. The reported values represent the averages of the fitting parameters obtained on three experimental decays. The errors are given by the corresponding standard deviations. Calculated mean fluorescence lifetime, τ_{av} , and fluorescence quantum yield relative to α -[Zn(BPEB)]), Φ_{fl} .

| Comm la | τ ₁ [ps] | $\tau_2 [ps]$ | τ ₃ [ps] | τ ₄ [ps] | τ _{av} [ps] | $\Phi_{ m fl}$ |
|--|---------------------------|---------------------------|---------------------------|---------------------------|----------------------|----------------|
| Sample | (f ₁) | (f ₂) | (f ₃) | (f ₄) | | |
| | | 182±3 | 617±19 | 1670±50 | 679.7 | 0.509 |
| Н ₂ врев | - | (0.34±0.02) | (0.46±0.02) | (0.20±0.02) | | (0.584) |
| α-[Zn(BPEB)] | | 180±7 | 627±20 | 1710±60 | 689.7 | 1 |
| | - | (0.32±0.02) | (0.49±0.02) | (0.19±0.02) | | |
| | | 173±5 | 544±9 | 1714±22 | 682.1 | 0.024 |
| [Fe ₂ (BPEB) ₃] | - | (0.29±0.01) | (0.50±0.01) | (0.21±0.01) | | |
| | 20±1 | 143±3 | 525±10 | 1960±24 | 441.7 | 0.015 |
| [Ni(BPEB)] | (0.44±0.01) | (0.20±0.01) | (0.21±0.01) | (0.15±0.01) | | |