Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Phosphine and Phosphine Oxide Groups in Metal-Organic Frameworks detected by P K-edge XAS

Flavien L. Morel,[a] *Sonia Pin,*[b§] *Thomas Huthwelker,*[b] *Marco Ranocchiari,*[b]

Jeroen A. van Bokhoven[*ab]

[a] *Department of Chemistry and Applied Biosciences, ETH Zürich, Vladimir-Prelog-Weg 1 , 8093 Zürich, Switzerland. E-mail: j.a.vanbokhoven@chem.ethz.ch; Tel: +41 44 632 5542*

[b] *Laboratory for Catalysis and Sustainable Chemistry, Paul Scherrer Institut, 5232 Villigen, Switzerland. E-mail: marco.ranocchiari@psi.ch; Tel: +41 56 310 5843*

[§] *Present address: Brembo S.p.a., Advanced R&D, Viale Europa 2, 24041 Stezzano (BG), Italy*

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1. Infrared spectroscopy

Infrared spectra were recorded in the range of 4000-400 cm^{-1} on a PerkinElmer 2000 FTIR spectrometer.

1.1. PPh_2-bdc and $POPh_2$-bdc

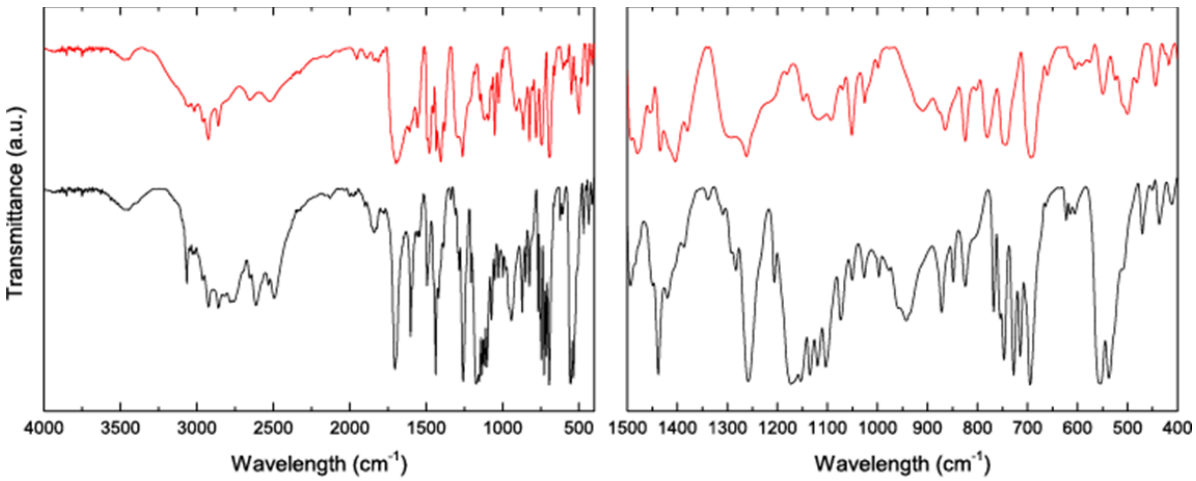

Figure S1. Infrared spectroscopy of PPh_2-bdc (red) and $POPh_2$-bdc (black). Full spectrum (left) and region of interest (right).

1.2. LSK-12 and LSK-15

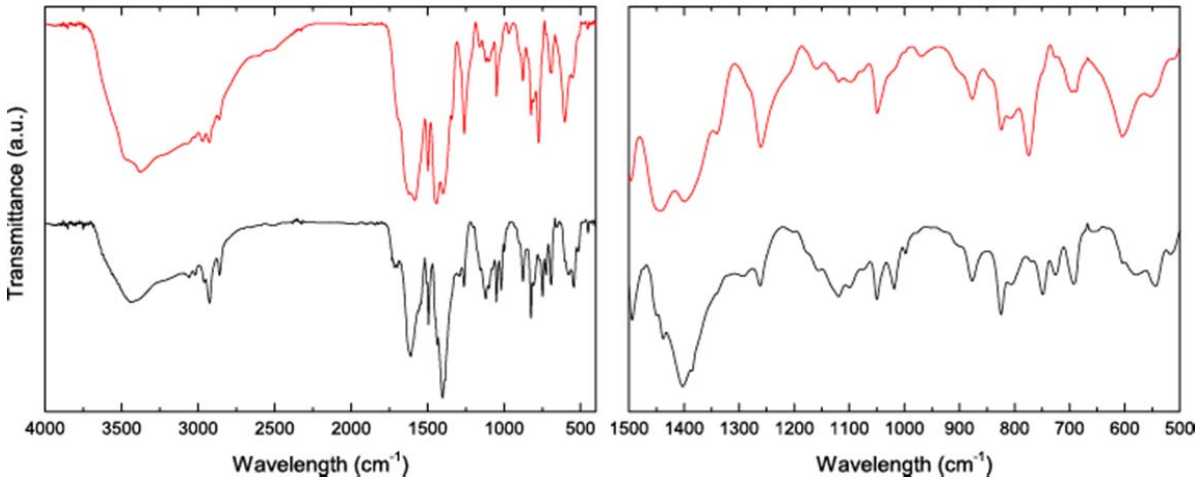

Figure S2. Infrared spectroscopy of SLK-15 (red) and LSK-12 (black). Full spectrum (left) and region of interest (right).

2. Summary of nitrogen physisorption experiments

Table S1. Nitrogen physisorption properties of LSK-12, LSK-15 and related materials.[1,2]

Materials	S_{BET} (m^2/g)	V_{pore} (cm^3/g)
LSK-12	3020	2.04
LSK-15	2692	1.32
MIL-101(Cr)	4100	1.90
MIL-101(Al)-NH_2	3099	1.53

3. Additional characterization of LSK-12

3.1. Powder X-ray diffraction pattern of LSK-12

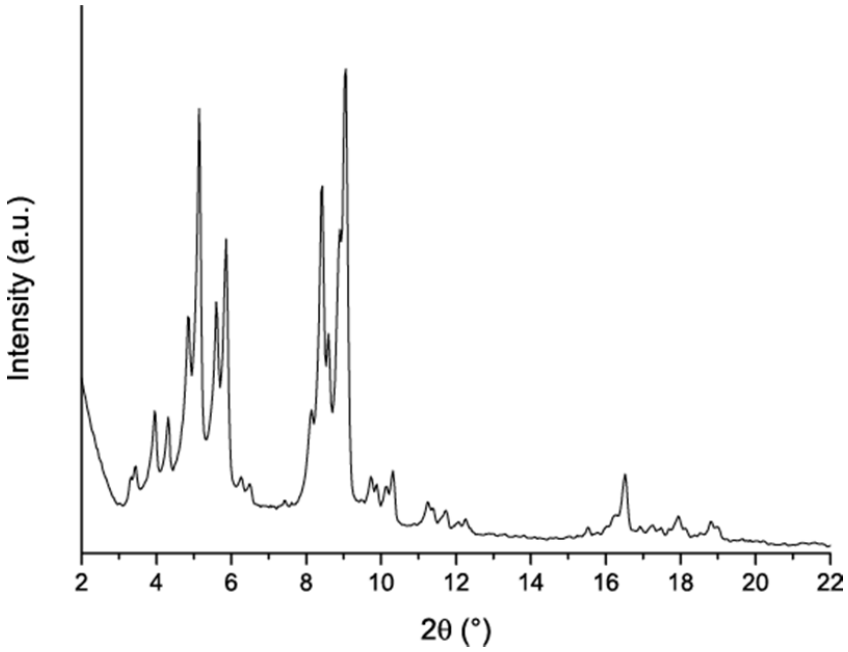

Figure S3. Powder X-ray diffraction pattern of LSK-12.

3.2. Liquid chromatography after digestion

LSK-12 (1 mg) was dissolved in a NaOH solution (400 µL 1 M) at 80 °C. Ethanol (400 µL) and phosphoric acid (60 µL, 85 % w/w) were added to the mixture, which was then filtered and analyzed in a Waters Acquity UPLC H-Class system equipped with a photodiodes array detector and a Waters BEH C18 (1.7 µm, 1.0 ×150 mm) column. The relative ratio bdc : $POPh_2$-bdc : PPh_2-bdc was equal to 20 : 1 : 0.

4. References

(1) Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F.; Dutour, J.; Surblé, S.; Margiolaki, I. A chromium terephthalate-based solid with unusually large pore volumes and surface. *Science* **309**, 2040–2042 (2005).

2) Hartmann, M.; Fischer, M. Amino-functionalized basic catalysts with MIL-101 structure. *Microporous Mesoporous Mater.* **164,** 38–43 (2012).