Supporting Information

Structure and Molecular Mobility of Phosphinine-based Covalent Organic Frameworks – Glass Transition of Amorphous COFs

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Synthesis:

CPSF-MeO and CPSF-EtO were synthesized according the Stille coupling protocol. The general reaction scheme is given in Figure S1.
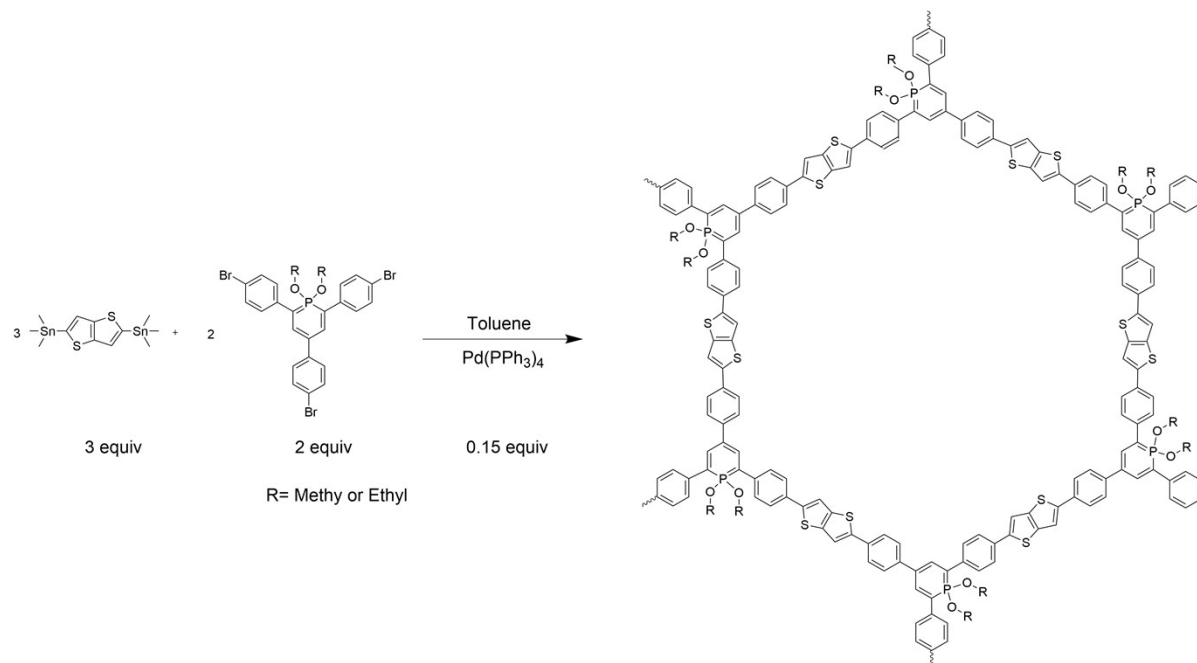

Figure S1: Chemical reaction scheme for the synthesis of CPSF-MeO and CPSF-EtO.

The synthesis product was filtered and then subsequently washed with tetrahydrofuran, dichloromethane and methanol. The material was further purified by Soxhlet extractions using subsequently tetrahydrofuran and methanol to remove the catalyst and unreacted components. To characterize the coupling reaction elemental analysis/ Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) regarding the elements C, H, P, Pd, Sn, and Br was carried out. This analysis reveals a low content of Sn and Br indicating an almost complete coupling (see Table S1).

Table S1a: Elemental analysis/ICP-OES for CPSF-MeO

	C [%]	N [%]	O [%]	H [%]	P [%]	S [%]	Pd [%]	Br [%]	Sn [%]
Theoretical	69.1	0	5.4	3.9	5.2	16.3	0	0	0
Measured	61.33	0	-	3.63	3.70	12.64	0.07	2.71	1.11

Table S1b: Elemental analysis/ICP-OES for CPSF-EtO

	C [%]	N [%]	O [%]	H [%]	P [%]	S [%]	Pd [%]	Br [%]	Sn [%]
Theoretical	69.87	0	5.17	4.41	5.01	15.54	0%	0	0
Measured	61.33	0.09	-	4.03	3.99	13.58	0.06	2.59	0.71

^{31}P magic angle spinning (MAS) solid-state NMR (ssNMR) and ^{13}C cross polarization magic angle spinning (CP-MAS) ssNMR

CPSF-MeO:

^{31}P magic angle spinning (MAS) solid-state NMR (ssNMR) is shown in Figure S2a. The two peaks at $\delta = 63.79$ and 20.78 ppm in the ^{31}P MAS ssNMR spectrum of CPSF-MeO are assigned to the ring-P of the λ^5-phosphinine moiety and to Ph_3PO, respectively. Residues of Ph_3PO are a side-product of the decomposition of $Pd(PPh_3)_4$ catalyst.[1]

The ^{13}C cross polarization magic angle spinning (CP-MAS) ssNMR spectra of CPSF-MeO is depicted in Figure S2b. The characteristic peaks for λ^5-phosphinine are at 113.6 (para-C of P), 94.84 / 91.50 ppm (ortho-C of P) and 47.60 ppm (C in MeO).
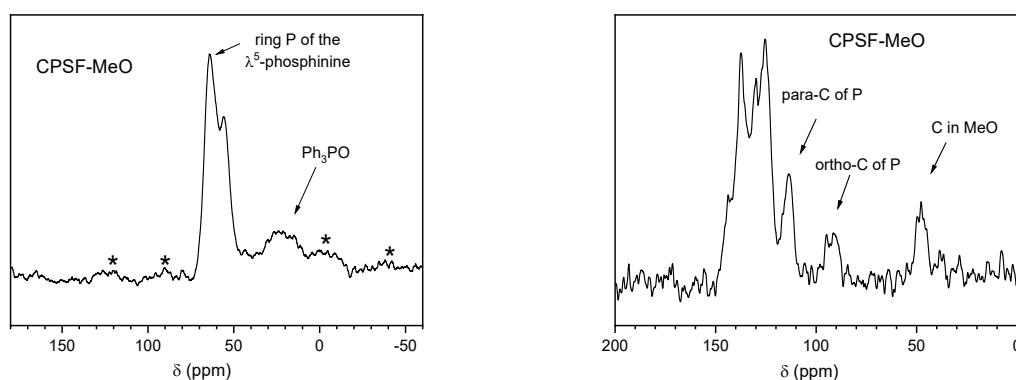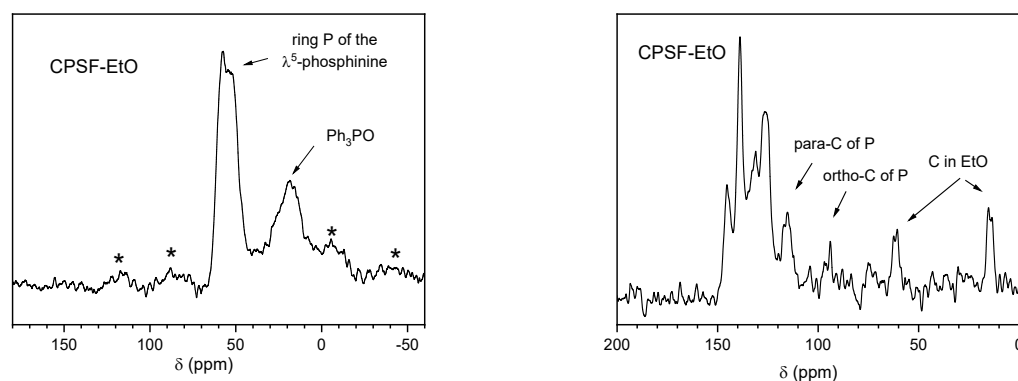

Figure S2: ^{31}P magic angle spinning (MAS) solid-state NMR (ssNMR) (left) and ^{13}C cross polarization magic angle spinning (CP-MAS) ssNMR spectra (right) of CPSF-MeO.

CPSF-EtO:

^{31}P magic angle spinning (MAS) solid-state NMR (ssNMR) is shown in Figure S3a. The two peaks at $\delta = 63.79$ and 57.91 ppm in the ^{31}P MAS ssNMR spectrum of CPSF-MeO are assigned to the ring-P of the λ^5-phosphinine moiety and to Ph_3PO, respectively. Residues of Ph_3PO are a side-product of the decomposition of $Pd(PPh_3)_4$ catalyst.[1]

The ^{13}C cross polarization magic angle spinning (CP-MAS) ssNMR spectra of CPSF-MeO is depicted in Figure 3b. The characteristic peaks for λ^5-phosphinine are at 115.6 ppm (para-C of P), 94.00 ppm (ortho-C of P), 60.40 and 15.17 ppm (C in EtO).[1]

Figure S3: [31]P magic angle spinning (MAS) solid-state NMR (ssNMR) (left) and ^{13}C cross polarization magic angle spinning (CP-MAS) ssNMR spectra (right) of CPSF-EtO.
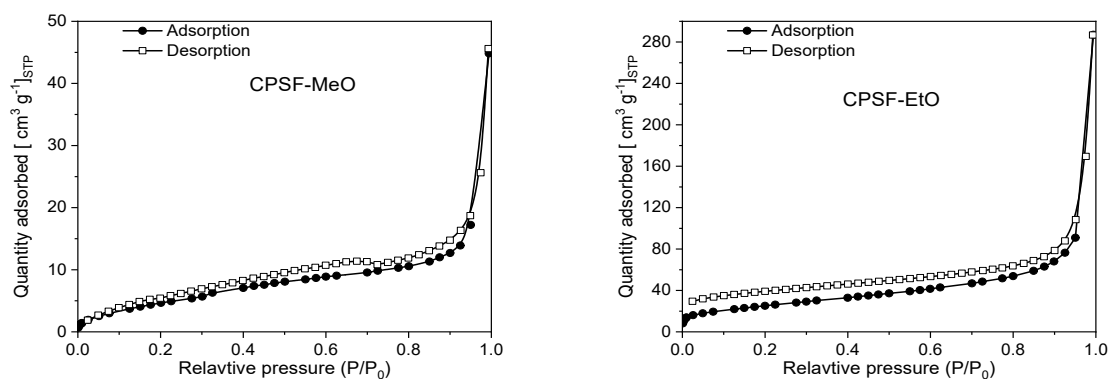
Adsorption measurements:

Figure S4: Nitrogen adsorption and desorption measurements at 77 K for CPSF-MeO (left) and CPSF-EtO (right). STP refers to standard conditions. The lines are guides to the eyes.
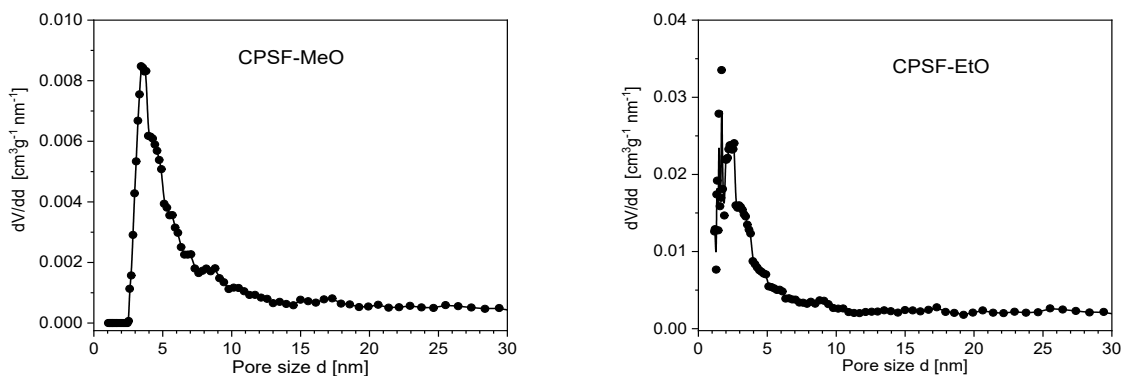
Figure S5: Pore size distribution for CPSF-MeO (left) and CPSF-EtO (right). The data were estimated by the NLDFT method. The lines are guides to the eyes.

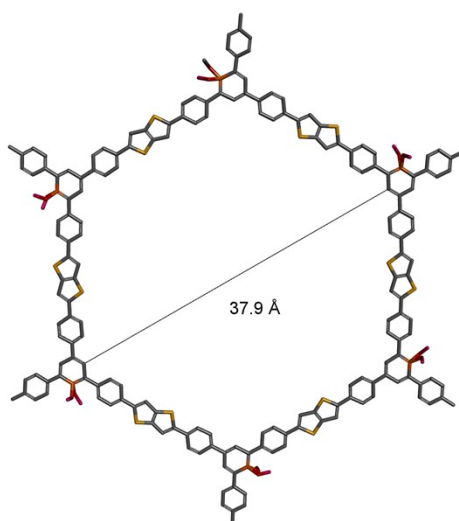## Theoretical pore size:

37.9 Å

Figure S6: Theoretical pore size of the macrocycle.

Conventional Differential Scanning Calorimetry:

DSC measurements were performed by a DSC 8500 instrument (Perkin Elmer, USA) with heating and cooling rates of 10 K/min Nitrogen was used as purge gas at a flow rate of 20

L/min. Baseline corrections were conducted by measuring an empty pan under the same condition than the sample. Indium was used as calibration standard.
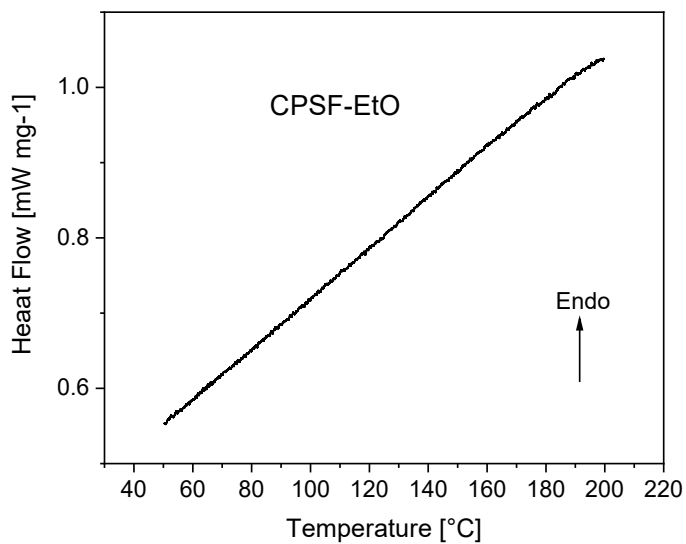

Figure S7: Conventional DSC measurement for CPSF-EtO, second heating run. The heating rate was 10 K/min.

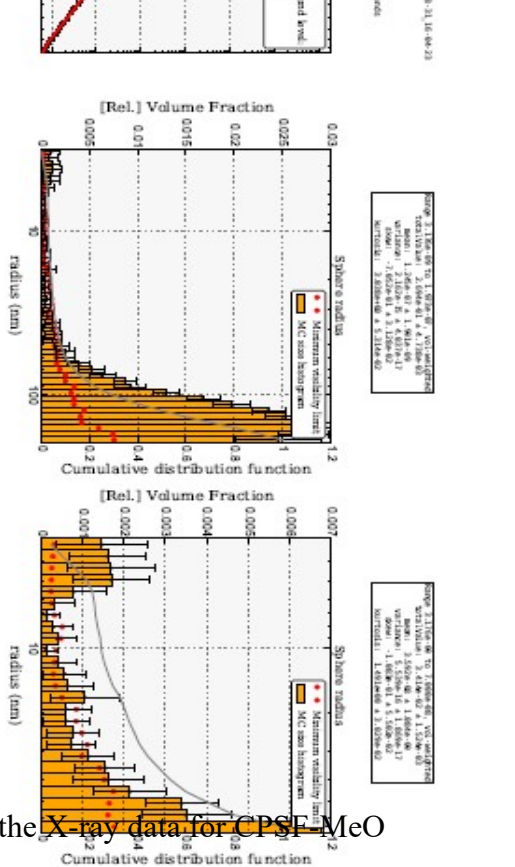**Analysis of the X-ray measurements:**

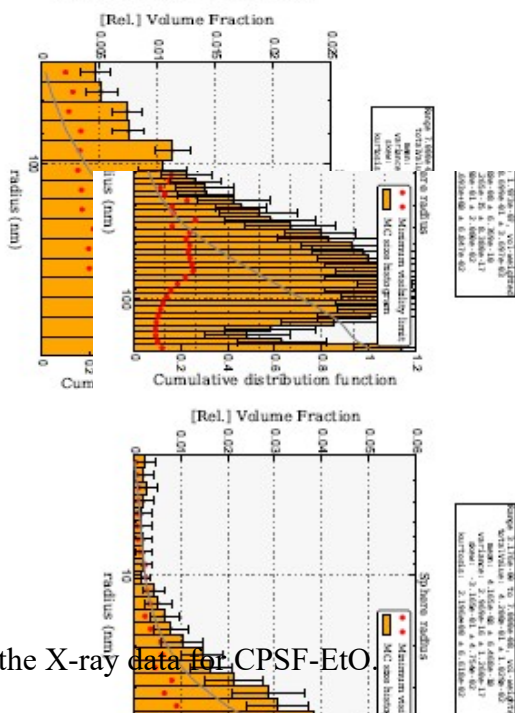Figure S8: Monte-Carlo fitting analysis of the X-ray data for CPSF-MeO

Figure S9: Monte-Carlo fitting analysis of the X-ray data for CPSF-EtO.

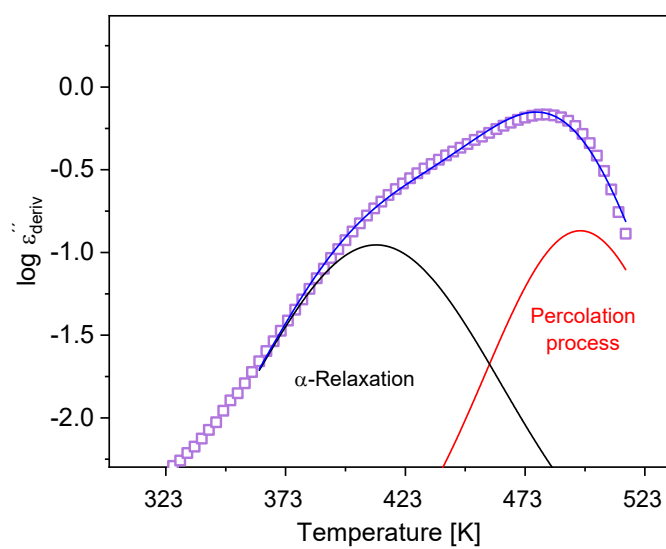**Analysis of the dielectric spectra in the temperature domain**

Figure S10: Analysis of the dielectric spectra in the temperature domain for CPSF-EtO at a frequency of 9.7 Hz.

Estimation of the ratio of the number of layers in the COF aggregates:

For the estimation of the ratio of the layers in both COF materials cylindrical pores were assumed. The surface area of a cylinder is given by

$$A_c = 2\pi r(r + h) \tag{Equ. S1}$$

where r is the radius of the cylinder and h it is height. Identifying the BET surface area value with the surface of the cylinder and r with the radius of the pores the following ratio can be given, considering approximately the same pore radius for both materials

$$\frac{BET\ surface\ area_{CPSF-EtO}}{BET\ surface\ area_{CPSF-MeO}} = \frac{2\pi r(r + h_{CPSF-EtO})}{2\pi r(r + h_{CPSF-MeO})} = \frac{r + h_{CPSF-EtO}}{r + h_{CPSF-MeO}}. \tag{Equ S2}$$

The height of the pore can be expressed by

$$h_{COF} \approx n_{COF} h_{Single\ COF\ layer} \tag{Equ S3}$$

equation S2 is rewritten to

$$\frac{BET\ surface\ area_{CPSF-EtO}}{BET\ surface\ area_{CPSF-MeO}} = \frac{r + n_{CPSF-EtO} h_{Single\ CPSF-EtO\ layer}}{r + n_{CPSF-MeO} h_{Single\ CPSF-MeO\ layer}} \tag{Equ S4}$$

Assuming further that the height of both single COF layers is approximately the same and that $r < h_{COF}$ equation S4 simplifies to

$$\frac{BET\ surface\ area_{CPSF-EtO}}{BET\ surface\ area_{CPSF-MeO}} \approx \frac{n_{CPSF-EtO}}{n_{CPSF-MeO}}; \frac{92.2\ m^2\ g^{-1}}{21.5\ m^2\ g^{-1}} \approx 4.3 \tag{Equ S5}$$

Reference:

[1] Huang, J.; Tarábek, J.; Kulkarni, R.; Wang, C.; Dračínský, M.; Smales, G. J.; Tian, Y.; Ren, S.; Pauw, B. R.; Resch-Genger, U.; Bojdys, M. J. A π-Conjugated, Covalent Phosphinine Framework. *Chemistry–A European Journal* **2019** *25*, 12342-12348.