

# Porphyrin based metal-organic frameworks with record sensitivity in optical oxygen sensing

Tobias Burger,<sup>1</sup> Christian Winkler,<sup>2</sup> Irene Dalfen,<sup>1</sup> Christian Slugovc,<sup>3,\*</sup>  
Sergey M. Borisov<sup>1,\*</sup>

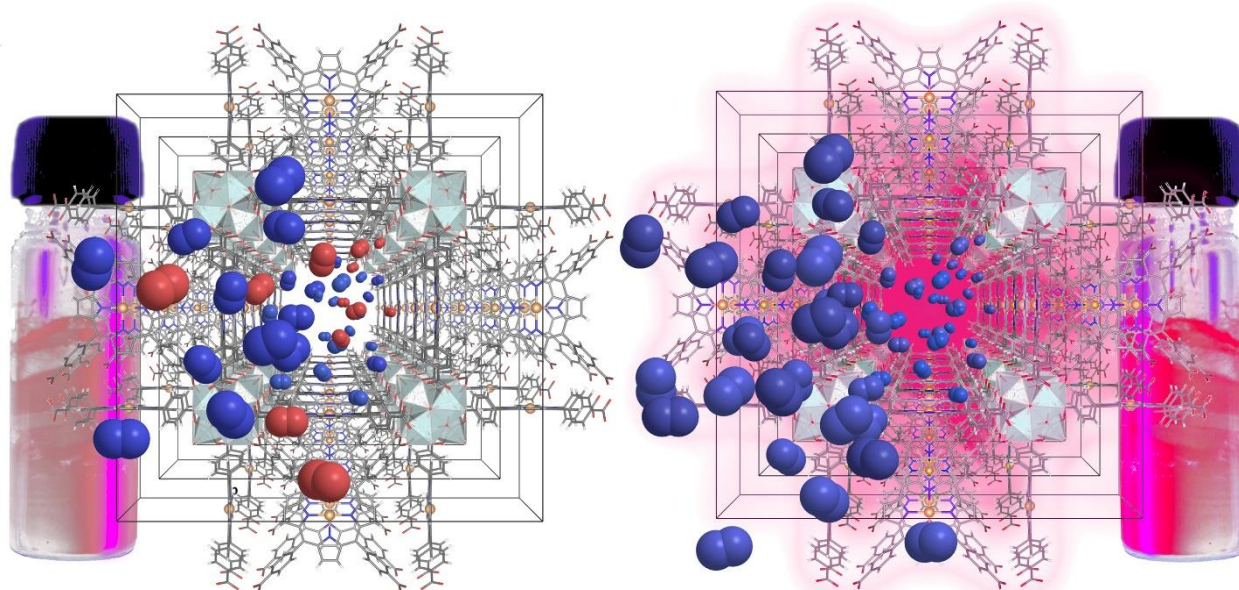
<sup>1</sup> Graz University of Technology, Institute of Analytical Chemistry and Food Chemistry; Stremayrgasse 9; 8010 Graz; Austria

<sup>2</sup> Graz University of Technology, Institute of Solid State Physics; Petersgasse 16; 8010 Graz; Austria

<sup>3</sup> Graz University of Technology, Institute of Chemistry and Technology of Materials; Stremayrgasse 9; 8010 Graz; Austria

**Abstract:** The optical oxygen sensing capabilities of the porphyrin-based metal-organic frameworks, PCN-224, Pt(II)PCN-224 and Pd(II)PCN-224 were investigated. The bimolecular quenching constants ( $k_q$ ) of 37000 (PCN-224), 6700 (Pd(II)PCN-224) and 3900 Pa<sup>-1</sup>s<sup>-1</sup> (Pt(II)PCN-224) were found and reveal an exceptionally high oxygen-permeability for these materials. A fast gas transport within the network, large pore sizes, electronic and spatial isolation of the porphyrin indicator in the framework are held responsible for the unprecedentedly high  $k_q$  values. PCN-224 shows 6.7 ns fluorescence lifetime and the fluorescence in air is quenched by 4.2-fold. The metal-organic frameworks based on phosphorescent Pt(II) and Pd(II) porphyrins possess significantly longer decay times of 18.6 and 390  $\mu$ s, respectively, and are suited to detect oxygen in trace and ultra-trace ranges with limits of detection of 1 and 0.015 Pa, respectively.

Apart from free-standing crystals, also metal-organic frameworks supported on different fibrous substrates (poly(acrylonitrile) nanofibers, glass fibres), and flat substrates (TLC silica-gel, poly(amide) filter) were prepared in order to provide oxygen sensor materials of practical use. Electrospun and thermally treated poly(acrylonitrile) nanofibers were proven to be particularly favourable and the resulting composite material exhibited the same sensitivity as the free crystals. All sensing materials show reversible cross-talk to humidity at levels up to 53 % relative humidity but demonstrate a drastic decrease of oxygen sensitivity at high humidity levels and when exposed to water.



**Keywords:** metal-organic framework; luminescence, platinum; palladium; porphyrin

## Introduction

Widely applied optical oxygen sensors rely on quenching of the luminescence of an indicator by molecular oxygen.<sup>1</sup> Although the state-of-the-art sensors are well suited for most applications and some are commercially available, there is still considerable interest for further improvements in applications like trace or ultra-trace sensing<sup>2</sup> or measurements under harsh conditions (high pressures, temperatures, presence of organic solvents etc.).<sup>3,4</sup> Conventional sensors are made in the form of planar foils or of fibre-optic setups and are commonly prepared by immobilization of molecular indicators into an oxygen-permeable matrix that acts as a support and solvent for the dye and a permeation-selective membrane. This is also true for nanoparticle-based oxygen probes used in biological and medical research,<sup>5</sup> but indicators conjugated to proteins<sup>6</sup> and peptides<sup>7,8</sup> proved very successful alternatives. The performance of matrix-immobilized sensors is mainly determined by the properties of the indicator (spectral properties, photostability, luminescence decay time) and the matrix (chemical stability, oxygen permeability, permeation selectivity). Compatibility of both materials is important since aggregation of the indicator negatively affects the sensor performance. The sensitivity of optical oxygen sensors is mainly governed by two parameters: luminescence decay time of the indicator and oxygen permeability of the matrix.<sup>9</sup> Considerably long decay times are required to achieve sufficient sensitivities in common matrices which explains why fluorescent dyes, popular in the early era of oxygen sensor development,<sup>1,10</sup> are rarely used nowadays. Among numerous phosphorescent indicators explored metalloporphyrins are probably the most popular representatives.<sup>10,11</sup> Palladium(II) and platinum(II) are almost exclusively used as central atoms; their porphyrin complexes possess phosphorescence lifetimes in order of tens and hundreds of microseconds, respectively. Immobilization of these indicators in polymers with moderate oxygen permeability such as polystyrene and its copolymers with acrylonitrile, poly(methyl methacrylate) etc. results in sensors operating at ambient conditions. On the other hand, highly gas-permeable matrices are required for preparation of sensors for traces of oxygen. These include polymers with high free volume such as silicone rubber,<sup>12</sup> perfluorinated polymers of Teflon AF<sup>13</sup> and Hyflon AD<sup>14</sup> series and poly(1-trimethylsilyl-1-propyne),<sup>15</sup> which is the polymer with the highest oxygen permeability ever reported. In a different approach, the indicators are physically adsorbed<sup>16</sup> or covalently<sup>13</sup> immobilized onto the surface of porous materials such as silica-gel<sup>13</sup> or mesoporous silica<sup>17,18</sup> where the dye is fully accessible to the interaction with molecular oxygen.

Another promising way to construct in first sight “matrix-free” indicators is to incorporate the dyes into metal-organic frameworks (MOFs). MOFs are typically crystalline materials that generally consist of metal nodes and organic linkers and are usually characterized by an extremely high porosity.<sup>19</sup> The great variety of organic linkers and metal nodes enables a huge structural diversity of MOFs, including the synthesis of luminescent variants.<sup>20</sup> Due to the permanent porosity and high accessibility to gases in the framework, these materials are promising for sensing applications<sup>21</sup> including oxygen quantification.<sup>22</sup> The oxygen sensing-unit can be either a structural element of the porous network or, alternatively, be incorporated into the pores during synthesis<sup>23</sup> or via post-synthetic incubation.<sup>24</sup> Incorporation into the pores during synthesis does not allow for much control over the distribution of the indicator dye within the framework that is reflected in distinctly nonlinear Stern-Vollmer plots due to different oxygen accessibilities within the crystal.<sup>23</sup> Additionally, such materials may be prone to leaching of the indicator out of the pores although it can be minimized via design of the pore structure.<sup>25</sup> On the other hand, incorporation of a sensing element as a MOF building block not only eliminates leaching but also potential aggregation of dyes that may negatively affect the luminescent and sensing properties. Porphyrins are excellent organic linkers for the construction of MOFs and many different frameworks have been described over the last decades.<sup>26,27</sup> Unfortunately, many of them are prone to hydrolysis<sup>28</sup> and are therefore of limited interest for sensing applications under ambient conditions. One well-described and hydrolytically considerably stable porphyrin-based MOF is PCN-224.<sup>29</sup> PCN-224 consists of Zr<sub>6</sub> clusters which are connected by tetrakis-(4-carboxyphenyl) porphyrin (H<sub>2</sub>TCPP) as organic linker and is sufficiently insoluble in most common solvents as well as hydrolytically stable in a broad pH range (1 to 11). This MOF has a permanent porosity with a reported BET surface of 2600 m<sup>2</sup> g<sup>-1</sup> and large pore sizes of 1.9 nm in

diameter.<sup>29</sup> These properties renders PCN-224 and closely related MOFs attractive for many applications such as (photo)catalysis,<sup>30,31,32</sup> photodynamic therapy<sup>33,34</sup> or drug delivery.<sup>26,35,36</sup> However, the luminescence properties of the PCN-224 in context of oxygen sensing in the gas phase have not been investigated. Only the Pt(II) derivative of PCN-224, Pt(II)PCN-224, was used for real-time monitoring of dissolved oxygen in aqueous dispersion. The MOF was demonstrated to respond to oxygen in physiologically relevant concentration range showing about 3-fold quenching of luminescence intensity in air-saturated conditions.<sup>37</sup> Such sensitivity is comparable to that of the materials prepared by immobilization of Pt(II) porphyrins in polystyrene or poly(methylmethacrylate) and is much lower than it would be expected from highly porous MOFs.<sup>38,39,40</sup>

In this work we investigate the effect of molecular oxygen on luminescent properties of three MOFs: the fluorescent PCN-224 based on the metal-free porphyrin linker and the phosphorescent analogues Pt(II)PCN-224 and Pd(II)PCN-224. We will show that the porous framework ensures excellent accessibility of the porphyrin emitters to molecular oxygen and thus unprecedentedly high bimolecular quenching constants. Very efficient quenching in the gas phase is observed already for fluorescent PCN-224 MOF, whereas the luminescence of the metalated analogues is quenched by traces of molecular oxygen. Pd(II)PCN-224 MOF belongs to one of the most oxygen sensitive materials reported so far. In fact, the sensitivity of the Pd(II)PCN-224 MOF exhibiting a Stern-Volmer constant ( $K_{SV}$ ) of 2610 kPa<sup>-1</sup> surpasses by far the sensitivity of known trace oxygen sensors based on Pd(II) porphyrins immobilized into porous silica-gel matrix ( $K_{SV}$  of 67 kPa<sup>-1</sup>).<sup>13</sup> In this contribution we will also show how the MOFs can be conveniently immobilized onto different materials a step necessary to improve their handling in sensing applications.

## Materials and Methods

### Chemicals and Materials

5,10,15,20-Tetrakis-(4-carboxyphenyl)-21,23H-porphyrin (H<sub>2</sub>TCPP) was purchased from Porphyrin-Laboratories, (Porphyrin-Laboratories GmbH, Gleschendorf, Germany, [www.porphyrin-laboratories.com](http://www.porphyrin-laboratories.com)). Zirconyl chloride octahydrate (ZrOCl<sub>2</sub> · 8H<sub>2</sub>O), N,N-dimethylformamide (DMF), acetic acid, potassium chloride and magnesium chloride were obtained from Roth ([www.carlroth.com](http://www.carlroth.com)). Magnesium nitrate was acquired from Merck ([www.merckmillipore.com](http://www.merckmillipore.com)). Poly(acrylonitrile) (PAN,  $M_w = 150000$  g/mol) was from obtained from Sigma Aldrich ([www.sigmaaldrich.com](http://www.sigmaaldrich.com)). Hyflon® AD 60 was obtained from Solvay ([www.solvay.com](http://www.solvay.com)) and perfluorodecalin was from Fluorochem ([www.fluorochem.co.uk](http://www.fluorochem.co.uk)). The polyamide (PA) substrate was a Biotyne Plus® Transfer membrane with 0.45 µm pore size from Pall (Pall Corporation, Port Washington, USA, [www.pall.com](http://www.pall.com)). Glass micro-fiber filters (Whatman, Ø 4.7 cm) were purchased from Sigma Aldrich ([www.sigmaaldrich.com](http://www.sigmaaldrich.com)). Silica-gel coated TLC-plates and acetone were from VWR ([www.vwr.com](http://www.vwr.com)). Polyethylene terephthalate (PET) foils (125 µm) (MELINEX 506) were supplied by Pütz (Pütz GmbH Co. Folien KG, Taunusstein, Germany; [www.puetz-folien.com](http://www.puetz-folien.com)). Pt(II)TCPP was prepared similar to a previously described procedure<sup>41</sup> and Pd(II)TCPP was prepared following a previously described microwave-assisted synthesis.<sup>42</sup> Poly(trimethylsilylpropyne) (PTMSP) was synthesized according to literature.<sup>43</sup>

**Synthesis of PCN-224.** The synthesis of PCN-224 relies on a published recipe.<sup>44</sup> In a typical experiment H<sub>2</sub>TCPP (6.2 mg, 7.8 µmol) and ZrOCl<sub>2</sub> · 8H<sub>2</sub>O (32.2 mg, 0.1 mmol) were dispersed in a mixture of DMF (12.5 mL) and acetic acid (6.2 mL). The dispersion was sonicated for 20 min in a 50 mL round bottom flask and kept at 65 °C for 72 h. After cooling to ambient temperature, the PCN-224 crystals were collected by centrifugation and washed three times with DMF (10 mL) and three times with acetone (10 mL). For removal of residual DMF, the solid was dispersed in acetone (3 mL) and volatiles were allowed to evaporate upon heating the dispersion placed on a watch glass on a hotplate operated at 65 °C. This operation was repeated 4 times. Finally, the material was dried under vacuum at 65 °C until constant weight was reached.

**Synthesis of Pt(II)PCN-224 and Pd(II)PCN-224.** Pt(II)PCN-224 and Pd(II)PCN-224 were prepared analogously to PCN-224 using Pt(II)TCPP (7.7 mg, 7.8 µmol) or Pd(II)TCPP (7 mg, 7.8 µmol) as

the starting materials. At the final stage, the crystals were activated for 72 h in a glass vacuum oven (B-585 from Büchi, [www.buchi.com](http://www.buchi.com)) at 0.7 mbar and 120 °C.

**Immobilization of PCN-224.** In order to embed PCN-224 into a Hyflon AD 60 layer, a “cocktail” containing 1 % (w/w) of MOF powder and 10 % (w/w) Hyflon AD 60 in perfluorodecaline was prepared. This composition was knife-coated on PET support (thickness of the wet layer 25 µm) and dried in vacuum overnight.

Immobilization experiments on glass fibres, electrospun PAN nanofibers (see ESI for more details on preparation of electrospun nanofibers), silica-gel TLC substrate and PA filter sheets were done by directly growing the PCN-224 MOF on the substrate. The flat support materials were cut in squares of approximately 10x10mm and were immersed in the solution containing MOF precursors and the synthesis was carried out as described above. After the synthesis, residual reactants were removed by soaking the materials in DMF (10 mL) and acetone (10 mL). Each solvent was exchanged three times. The materials were dried in vacuum overnight.

**Instruments and Methods.** Powder X-ray diffraction (PXRD) measurements were performed at the XRD1 beamline at the Elettra Synchrotron in Trieste. This beamline has an operating wavelength of 1.4 Å with a beam size of 200 x 200 µm. The data was collected on a stationary Dectris Pilatus 2M detector which was mounted 400 mm away from the sample. The sample itself consisted of the MOF PCN-224 powder which was filled in a glass capillary (1.5 mm diameter and 0.02 mm wall thickness). All data were transformed to reciprocal space for analysis. All data conversion, treatment and analysis steps were performed with GIDVis.<sup>45</sup>

The morphology of the MOF powder samples was studied by a standard scanning electron microscope Jeol JSM-6490 LV ([www.jeol.de](http://www.jeol.de)). For preparing the samples the MOF powder was drop casted onto a Si wafer and carbon coated.

<sup>1</sup>H NMR spectra were recorded on a 300 MHz Avance III spectrometer from Bruker ([www.bruker.com](http://www.bruker.com)). Absorption spectra were measured on a Varian Cary 50 UV-VIS spectrophotometer from Agilent Technologies ([www.agilent.com](http://www.agilent.com)). Luminescence spectra were recorded on a Fluorolog-3 luminescence spectrometer from Horiba ([www.Horiba.com](http://www.Horiba.com)) equipped with a NIR sensitive photomultiplier R2658 from Hamamatsu ([www.hamamatsu.com](http://www.hamamatsu.com)). An optical fiber setup was used to guide the excitation light to a 10 mL Schlenk flask or a 3 mL screw-cap glass vial containing the MOF sample and to guide back the emission to the monochromator and photodetector. A custom-made 3D printed adapter (ESI, Fig. S20) was used for fixation of optical fibers. Luminescence decay times were acquired on the same spectrometer equipped with the DeltaHub module. The set-up was similar to the one used in the intensity measurements but a 453 nm laser diode “NanoLED” from Horiba ([www.horiba.com](http://www.horiba.com)) was used for excitation of PCN-224 and a 405 nm “SpectraLED” from Horiba ([www.horiba.com](http://www.horiba.com)) for excitation of Pt(II)PCN-224 and Pd(II)PCN-224. DAS-6 Analysis software was used for data analysis.

The composition of the calibration gas was adjusted with help of mass-flow controllers from Voegtlin ([www.voegtlin.com](http://www.voegtlin.com), Aesch, Switzerland) with the total flow rate of 200 mL min<sup>-1</sup>. For calibration of PCN-224 nitrogen (99.999% purity) and compressed air were used; for Pt(II)PCN-224 nitrogen of 99.9999% purity was mixed with the test gas (0.2% O<sub>2</sub> in nitrogen) and for Pd(II)PCN-224 nitrogen of 99.99999% purity was mixed with a test gas containing 20 ppm oxygen in nitrogen. All test gases were acquired from Linde gas ([www.linde-gas.de](http://www.linde-gas.de)). The temperature was 25 °C in all the experiments. In order to investigate the effect of humidity on the oxygen response of PCN-224, the gas compositions were bubbled through saturated aqueous solutions of MgCl<sub>2</sub> (33 % r.h.), Mg(NO<sub>3</sub>)<sub>2</sub> (53 % r.h.) and KCl (84 % r.h.) before entering the measurement compartment with MOF.

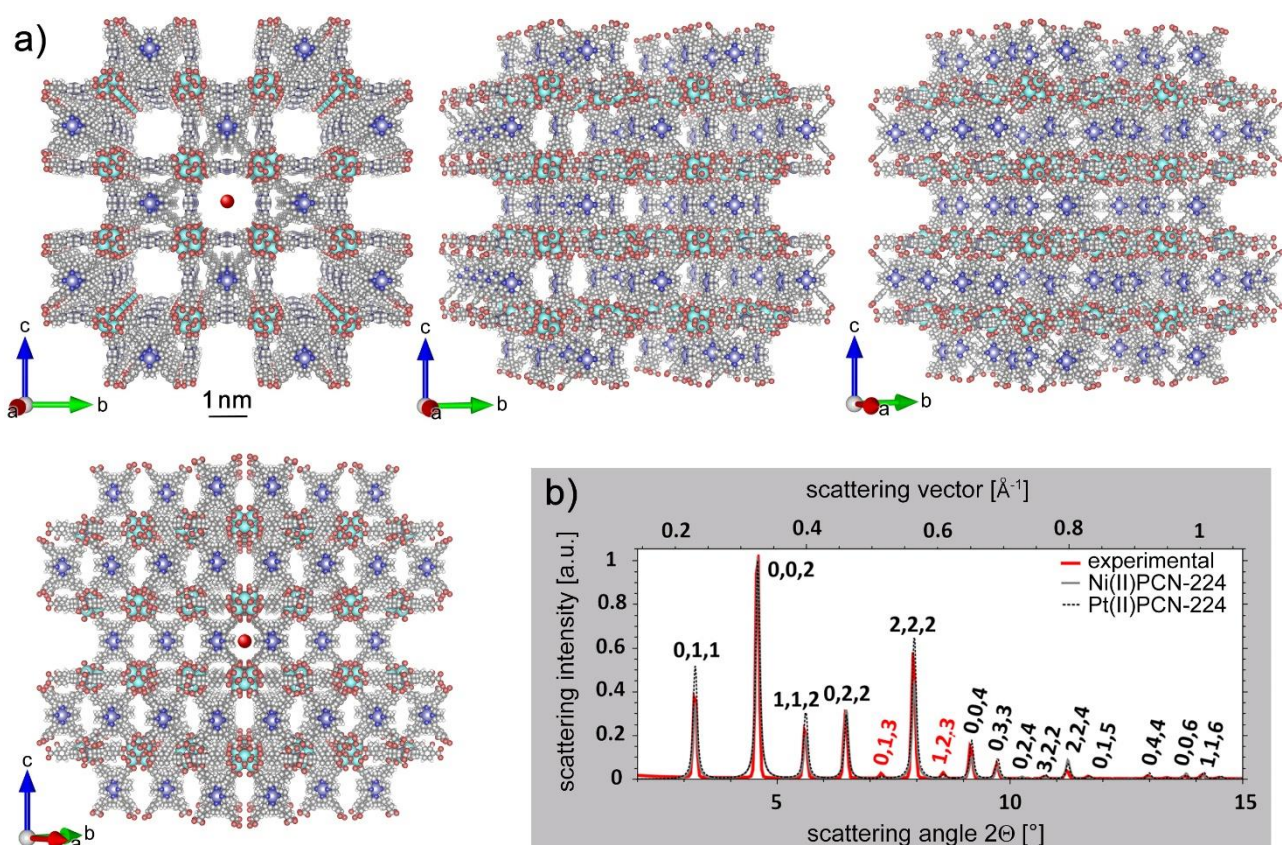
## Results and discussion

### Synthesis and structural characterization

The PCN-224 framework is grown from a solution of H<sub>2</sub>TCPP and zirconyl chloride octahydrate in a mixture of DMF and acetic acid.<sup>44</sup> The MOFs Pt(II)PCN-224 and Pd(II)PCN-224 were synthesized similarly using the Pt(II) and Pd(II) metalated porphyrin derivatives of H<sub>2</sub>TCPP. Residuals of DMF



were removed by repeated addition and evaporation of acetone and the MOFs were activated via prolonged treatment in vacuum at elevated temperature (72 h, 0.7 mbar, 120 °C).



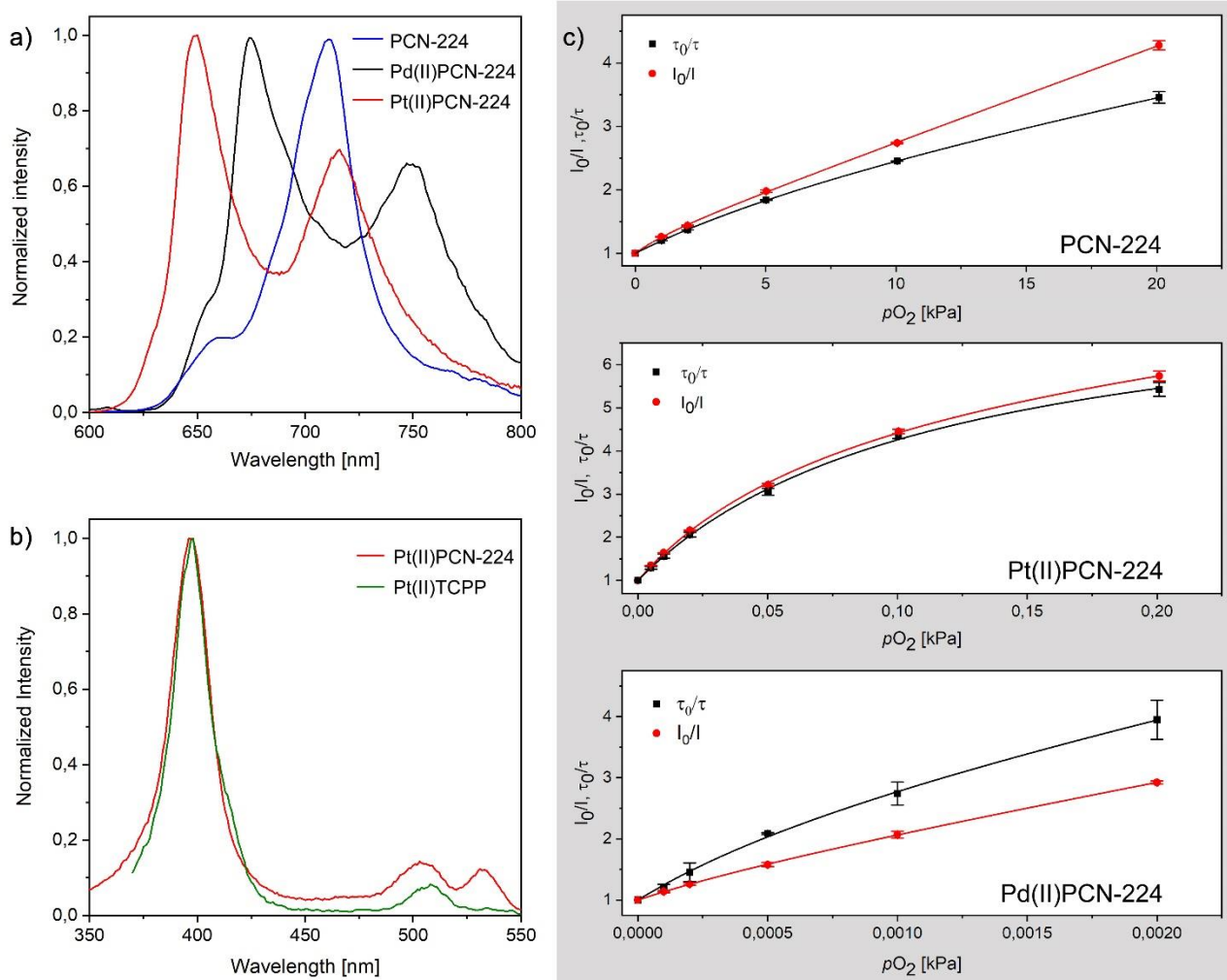
**Fig. 1.** a) Space fill-model of a metalated PCN-224 drawn in perspective view along the *a*-axis and rotated for 15, 30 and 45° around the *c*-axis showing the channels through the MOF and for comparison a red sphere representing the size of O<sub>2</sub> (based on the kinetic diameter of 346 pm) is shown. The visualization was done with the aid of VESTA.<sup>46</sup> b) Normalized PXRD data shown as a line graph. Experimental and calculated data for Pt(II)PCN-224 are plotted together with literature data for Ni(II)PCN-224. The data was extracted by integrating over the intensity of the experimental PXRD pattern and normalized to the maximum intensity. The data for the model structures was calculated by using the Mercury software.

The crystal size and morphology of PCN-224, Pt(II)PCN-224 and Pd(II)PCN-224 was investigated using scanning electron microscopy (Fig. S10, S11 and S12, respectively) and cubical crystals with an edge length of around 3–4 μm were obtained in all cases.

Powder X-ray diffraction studies were conducted and the obtained diffractograms were compared to those of PCN-224 and the analogous MOF based on the corresponding Ni(II) complex of TCPP (Ni(II)TCPP).<sup>29</sup> In both of these reference cases, the structure is cubic and belongs to the space group Im-3m (no. 229). Half of the edges of the Zr<sub>6</sub>-clusters forming the nodes are bridged by carboxylates from the TCPP ligands and the TCPP linker vacancies appearing in an ordered 3D checkerboard fashion (Fig. 1). To mimic the Pt(II) metalated MOF prepared here, the Ni(II) in the literature structure was changed for Pt(II). Fig. 1 shows that for both model systems Ni(II)PCN-224 and such a hypothetical Pt(II)PCN-224 the relative intensities of all peaks agree well with the relative intensities determined in the experiment. By comparing peak positions and relative intensities between the measured data and the data calculated for the literature structure (Fig. 1b for Pt(II)PCN-224 and ESI) it is concluded that the synthesized MOF exhibits the same structure as the PCN-224 family reported by Feng et al.<sup>29</sup> It is to note, that the published structures of PCN-221 (disordered variant of PCN-224) and MOF-525 (all edges of the Zr<sub>6</sub> cluster linked with TCPP derivatives) exhibit at scattering angles below 15° very similar patterns to that of PCN-224. However, only PCN-224 features the superstructure reflections observed at scattering angles of 3.2 and 5.5° so that the occurrence of ordered vacancies in the crystals discussed here is prevailing.<sup>47</sup>

## Luminescence of PCN-224 MOFs

Emission spectra of the three MOFs PCN-224, Pt(II)PCN-224 and Pd(II)PCN-224 are shown in Fig. 2a. In case of PCN-224 the emission is attributed to fluorescence due to decay time in the nanosecond time domain ( $\tau = 6.7$  ns in the absence of  $O_2$ ). In contrast, the MOFs based on Pt(II) and Pd(II) porphyrins show phosphorescence ( $\tau = 18.7$  and  $390$   $\mu$ s, respectively). As can be seen, the emission maximum for the PCN-224 in free powder is located at significantly longer wavelength (711 nm) than expected and only a small shoulder at around 660 nm is visible. Such distortion can be attributed to the inner-filter effect that is particularly strong in the MOF due to high concentration of the porphyrin and strong overlap between fluorescence and the  $Q_x$  (0,0) absorption band. The same phenomenon is well known for concentrated solutions of fluorescent emitters including porphyrins.<sup>48</sup> In accordance to the properties of Pt(II) and Pd(II) porphyrins in solutions, the emission maxima of Pt(II)PCN-224 is located at shorter wavelength ( $\lambda_{\max} = 645$  nm) compared to the corresponding Pd(II) MOF ( $\lambda_{\max} = 675$  nm).<sup>49</sup> The structure of PCN-224-based MOFs already suggests that individual porphyrin molecules are isolated and their aggregation, which causes pronounced changes of the optical properties<sup>49</sup> of the materials, is mitigated. Indeed, the excitation spectra recorded for Pt(II)PCN-224 (in aqueous dispersion) and the respective building block Pt(II)TCPP (in aqueous solution) are very similar (Fig. 2b). Thus, the arrangement of porphyrin molecules in MOF appears to be an efficient strategy to obtain systems with high concentration of the luminophore without its aggregation.



**Fig. 2.** Luminescence spectra of MOFs; a) emission spectra of PCN-224 ( $\lambda_{exc}$  420 nm), Pt(II)PCN-224 ( $\lambda_{exc}$  400 nm) and Pd(II)PCN-224 ( $\lambda_{exc}$  400 nm) powders under anoxic conditions; b) excitation spectra of Pt(II)TCPP in aqueous solution and Pt(II)PCN-224 in aqueous dispersion ( $\lambda_{em}$  650 nm) under anoxic conditions. c) Stern-Volmer plots for PCN-224, Pt(II)PCN-224 and Pd(II)PCN-224 at 25 °C and dry gas atmosphere.

## Luminescence quenching by molecular oxygen

Luminescence of the three MOFs was found to be quenched by molecular oxygen (Fig. 2c). Whereas such behaviour was expected for the MOFs based on phosphorescent Pd(II) and Pt(II) porphyrins it is very unusual in case of PCN-224 formed by a fluorescent free-base porphyrin. In fact, fluorescent dyes are usually seen as “immune” to oxygen quenching due to their short emission lifetimes. Luminescence quenching by molecular oxygen is of dynamic nature and the Stern-Volmer equation (1) is used to adequately describe the quenching dependency in case of dissolved dyes. In these conditions, the decrease of the luminescence intensity is identical to the decrease of the decay time and both show linear dependency on the concentration of the quencher [O<sub>2</sub>].

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + K_{SV} \cdot [O_2] = 1 + k_q \cdot \tau_0 \cdot [O_2] \quad (1)$$

where  $I_0$  and  $\tau_0$  are the luminescence intensity and luminescence decay time under oxygen-free conditions,  $I$  and  $\tau$  the same parameters at a certain oxygen concentration,  $K_{SV}$  is the Stern-Volmer constant and  $k_q$  the bimolecular quenching constant. For indicator dyes immobilized into different matrices (most commonly polymers) such ideal dependency is rarely found. Instead, the dependencies are not linear and not fully identical for the luminescence intensity and the decay time. This is explained by heterogeneity of the environment in which individual indicator molecules are located that results in different oxygen quenchability. As can be seen from Fig. 2c, the same is true for the three MOFs. Such behaviour can be due to combination of several factors including (i) defects in the MOF, (ii) different oxygen accessibility of the porphyrin molecules that are located on the surface of an individual crystal and on the inner pores, (iii) blocking of some pore channels for instance with residual solvent molecules that are trapped inside and hinder oxygen transport. Therefore, the so called “two site model”<sup>50</sup> (Eq. 2) was used to fit the experimental data. The model postulates localization of the indicator in two environments of significantly different oxygen permeability and although is physically meaningful only for the luminescence intensity, it also adequately fits the decay time plots.

$$\frac{I_0}{I} = \left( \frac{f}{1 + K_{SV1} \cdot [O_2]} + \frac{1-f}{1 + K_{SV2} \cdot [O_2]} \right)^{-1} \quad (2)$$

where  $f$  is the proportion of the dye localized in the first environment,  $K_{SV1}$  and  $K_{SV2}$  are the Stern-Volmer constants for the first and the second environment. Fig. 2c shows that already for PCN-224 based on free-base porphyrin the quenching is very efficient: the fluorescence intensity decreases by more than 4-fold at air saturation comparing to anoxic conditions. For comparison, the quenching of the same magnitude is observed for Pt(II) porphyrins (such as Pt(II)TFPP) immobilized in polystyrene.<sup>51</sup> Notably, the luminescence decay time of Pt(II)TFPP in polystyrene<sup>51</sup> is roughly 4 orders of magnitude longer (55  $\mu$ s) than that of H<sub>2</sub>TCPP in PCN-224 (6.7 ns). Such an efficient quenching in a MOF can be explained by the fact that the porphyrin molecules are structural elements of the porous channels and thus are freely exposed to oxygen molecules that diffuse through them. In contrast, even in polymers with high free-volume polymer chains surround the indicator molecule partly protecting it from interaction with oxygen. It is therefore likely that oxygen permeability in PCN-224 is higher than that of poly(trimethylsilylpropyne) (PTMSP), a polymer with the highest oxygen permeability known.<sup>1</sup> To verify this, we embedded a lipophilic analogue of H<sub>2</sub>TCPP, namely 5,10,15,20-tetrakis-(4-methoxycarbonylphenyl)-21,23H-porphyrin (H<sub>2</sub>TMCPP) into PTMSP and investigated its oxygen response (Fig. S18). The Stern-Volmer constant obtained for this material is 0.073 kPa<sup>-1</sup> which is about 3.5-fold lower than for PCN-224 (0.25 kPa<sup>-1</sup>) despite the longer  $\tau_0$  of H<sub>2</sub>TMCPP in PTMSP (10.7 ns).

A known strategy to obtain highly oxygen-sensitive materials is to immobilize the indicator on the surface of a porous material such as silica-gel<sup>13</sup> or porous aluminium oxide.<sup>52</sup> In such materials the indicator molecules are exposed to the gas that more or less freely diffuses in the channels. As can be seen, the fluorescence of H<sub>2</sub>TCPP adsorbed on the surface of porous silica-gel is indeed significantly

quenched by molecular oxygen (Fig. S19). The Stern-Volmer constant of  $0.19 \text{ kPa}^{-1}$  is however lower than that for PCN-224 despite that the fluorescence decay time is higher for H<sub>2</sub>TCPP ( $\tau_0$  of  $\sim 10 \text{ ns}$ ) than for the porphyrin in the MOF ( $\tau_0 = 6.7 \text{ ns}$ ).

Considering the significant quenchability of PCN-224 that relies on a fluorescent dye we expected much stronger sensitivity for phosphorescent Pt(II)PCN-224 and Pd(II)PCN-224. Experimental results (Fig. 2c) show that this is indeed the case. In fact, in case of the former more than 5-fold decrease of luminescence intensity is observed at  $0.2 \text{ kPa pO}_2$ , whereas Pd(II)PCN-224 shows 3-fold quenching at only  $2 \text{ Pa}$  of oxygen. The limit of detection (LOD) was estimated with the blank value method (blank value + 3 x standard deviation). The LOD of Pt(II)PCN-224 was estimated to be  $1 \text{ Pa}$  and the LOD of Pd(II)PCN-224 was found to be  $0.015 \text{ Pa}$ . The materials based on Pt(II) and Pd(II) porphyrins thus cover trace and ultra-trace range of oxygen concentrations. Since the Stern-Volmer constant  $K_{SV}$  is proportional to the luminescence decay time of the indicator dye (eq. 1), it is interesting to compare the bimolecular quenching constant  $k_q = K_{SV}/\tau_0$  that reflects how efficient the diffusion of oxygen in the porous material is. The bimolecular quenching constant  $k_q$  was calculated using the  $K_{SV}$  values obtained from the luminescence intensity plots. The  $k_q$  constants were calculated to be  $37000$ ,  $3900$ , and  $6700 \text{ Pa}^{-1}\text{s}^{-1}$  for PCN-224, Pt(II)PCN-224 and Pd(II)PCN-224, respectively (Table 1). The bimolecular quenching constant is about one order of magnitude higher for the MOF based on fluorescent free-base porphyrin compared to the phosphorescent MOFs. This is in good agreement with the expectations of  $k_q$  approaching diffusion controlled limit ( $k_{diff}$ ) for fluorescent dyes (quenching of the excited singlet state) and  $1/9 k_{diff}$  for phosphorescent dyes (quenching of the excited triplet state) due to contribution of the spin-statistical factor.<sup>53</sup> For comparison, the  $k_q$  constant for H<sub>2</sub>TMCP embedded into PTMSP was calculated to be  $7200 \text{ Pa}^{-1}\text{s}^{-1}$ , that is about 5-fold lower than that for PCN-224 indicating that oxygen permeability of the MOF is significantly higher than that of PTMSP. Although the arrangement of the porphyrin molecules in PCN-224 may be particularly advantageous for efficient oxygen quenching, such property is not truly unique and may be characteristic for many other luminescent MOFs. In fact,  $k_q$  constant for the MOF MAFx-11<sup>54</sup> is  $19000 \text{ Pa}^{-1}\text{s}^{-1}$  which is about 2-fold lower than for PCN-224.

**Table 1.** Oxygen sensing properties of selected luminescent porous and non-porous materials.

Material	Matrix	$\tau_0$	$K_{SV} [\text{kPa}^{-1}]$	$k_q [\text{Pa}^{-1} \text{s}^{-1}]$	Ref.
SUMOF-6-Eu	porous	1 ms	0.07	0.07	55
EuNDC-MOF	porous	1.33 ms	0.13	0.1	56
Pt(II)Porph:UiO	porous	28 $\mu\text{s}$	0.13	4.7	57
Pd(II)OEP in PTMSP	polymer	$\sim 770 \mu\text{s}$	17	$\sim 22^d$	15
Pt(II)BP in silicone rubber	polymer	50 $\mu\text{s}$	1.4	28	12
Pt(II)TFPP in Hyflon AD60	polymer	92 $\mu\text{s}$	3.9	42	58
Pd(II)TFPP in Hyflon AD60	polymer	1180 $\mu\text{s}$	62.4	53	58
Pt(II)TFPP on silica-gel particles	porous	70 $\mu\text{s}$	3.7	53	13
Pt(II)OEP in PTMSP	polymer	$\sim 100 \mu\text{s}$	5.6	$\sim 56^d$	15
Pd(II)TFPP on silica-gel particles	porous	987 $\mu\text{s}$	67	68	13
Ru(II):MAF-34	porous	1.18 $\mu\text{s}$	0.21	178	23
Pyrene:MAF-4	porous	59 ns	0.06	1000	59
Pt(II)PCN-224	porous	18.6 $\mu\text{s}$	73 <sup>a</sup>	3900	This work
Pd(II)PCN-224	porous	390 $\mu\text{s}$ <sup>b</sup>	2610 <sup>a</sup>	6700 <sup>b</sup>	This work
H <sub>2</sub> TMCP in PTMSP	polymer	10 ns	0.072	7200	This work
MAF-X11	porous	14 ns	0.27	19000	54
H <sub>2</sub> TCPP on silica-gel particles	porous	10 ns	0.19	19000	This work
H <sub>2</sub> TCPP derivative on Al <sub>2</sub> O <sub>3</sub>	porous	$\sim 10 \text{ ns}$	0.23	$\sim 23000^c$	52
PCN-224	porous	6.7 ns	0.25 <sup>a</sup>	37000	This work

<sup>a</sup>  $K_{SV}$  fit according to eq. 2. For other fit parameters see Table S3; <sup>b</sup> Average quenching constant based on bi-exponential decay of two luminescent species; <sup>c</sup> calculated based on the estimated decay time reported in Ref. 52; <sup>d</sup> calculated based on the estimated decay times given in Ref. 1

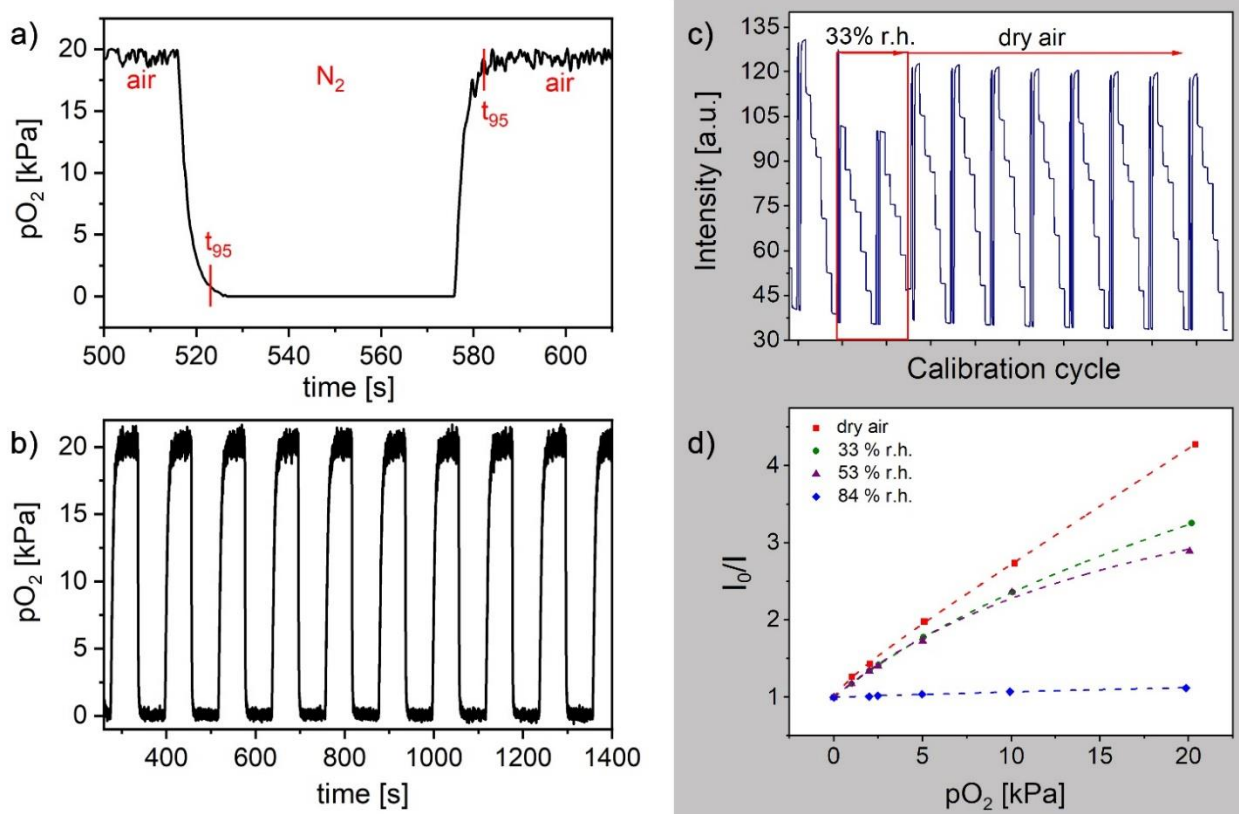
Table 1 summarizes the oxygen-sensing properties of various reported luminescent MOFs as well as selected porous and non-porous materials based on porphyrin indicators embedded in highly



oxygen-permeable matrices. It should be noted that the selection of materials was limited to those which allowed for the calculation of quenching constant  $k_q$ , i.e. contain the data on the luminescence decay time in the absence of the quencher. As can be seen, the bimolecular quenching constant  $k_q$  for most materials is much lower than that obtained for PCN-224, with the exception of MAF-X11<sup>54</sup> and H<sub>2</sub>TCPP adsorbed on other porous materials such as silica-gel and aluminium oxide. Comparison of the trace sensors based on Pt(II) and Pd(II) porphyrins reveals that these indicators immobilized in porous matrices (silica-gel) and highly oxygen-permeable non-porous polymers (Hyflon AD60, silicone rubber, PTMSP) show the  $k_q$  values in the range of 20-70 Pa<sup>-1</sup>s<sup>-1</sup> that is roughly 2 orders of magnitude lower than the bimolecular quenching constant obtained for Pt(II)PCN-224 and Pd(II)PCN-224. PCN-224 and its metalated analogues thus appear the most oxygen-permeable materials ever reported.

### Response times and reversibility

In a next step, response times and the reversibility were assessed. As shown in Fig. 3 the PCN-224 crystals fully reversibly respond to the alteration between oxygen-free atmosphere and air. The same holds for the two metalated MOF crystals. The dynamic response times  $t_{95}$  are within several seconds ( $\sim 6$  s going from anoxic conditions to air and  $\sim 7$  s in the reverse direction). Although such response times are comparable to most state-of-the-art oxygen sensors based on polymer-immobilized indicators, they appear to be much longer than expected from extreme oxygen permeability of the MOF. As will be discussed below these values are likely to be greatly overestimated due to the time needed for the gas atmosphere to be exchanged in the chamber with the crystals.



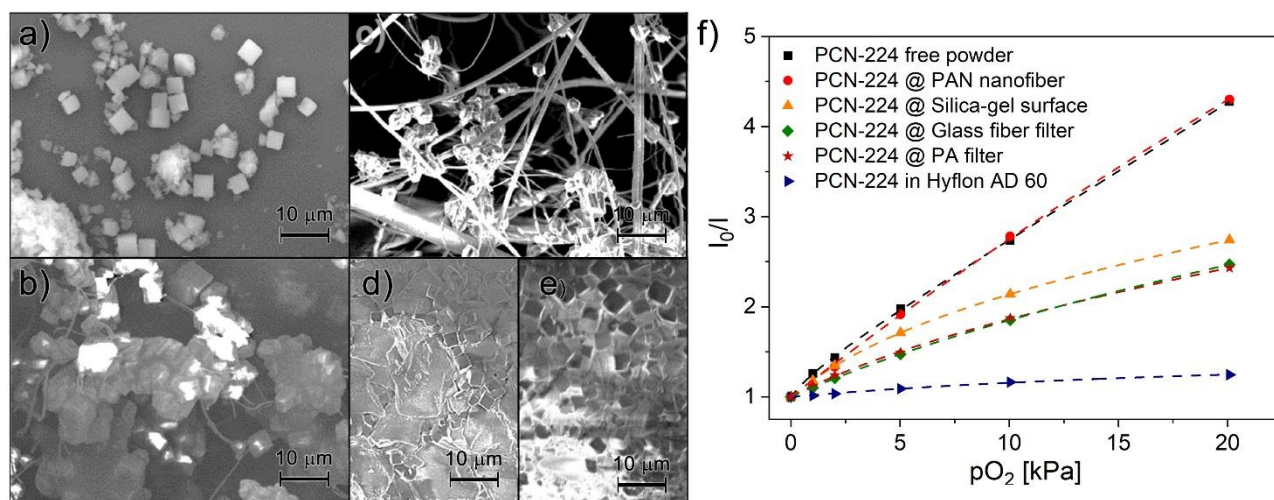
**Fig. 3.** Oxygen-sensing properties of free-standing PCN-224 crystals; a) dynamic response to alteration of gas atmosphere between nitrogen and air; b) 10 consecutive cycles of changing atmosphere between nitrogen and air demonstrating excellent repeatability and reversibility of the response. Grey box: Influence of humidity on the sensitivity of PCN-224; c) dynamic response of the material in dry air (first and last eight cycles) and at 33 % r.h. (cycles 2 and 3); d) Stern-Volmer plots for PCN-224 at varying relative humidity at 25°C.

### Influence of humidity on oxygen sensitivity

As was shown in Fig. 2c, Pt(II)PCN-224 is extremely sensitive to molecular oxygen in gas phase showing almost 6-fold quenching of phosphorescence intensity already at 0.2 kPa O<sub>2</sub>. On the other hand, the same material was reported to show about 3-fold quenching of luminescence intensity in air-saturated aqueous dispersion (~21 kPa O<sub>2</sub>).<sup>37</sup> Such drastic difference in the sensitivity (about 200-fold) can be explained by substitution of the gas phase inside the pores of the MOF by aqueous phase. Even for measurement in the gas phase, residual solvents including water can be trapped inside the MOF and thus hinder diffusion of oxygen through the pores. In fact, the extreme oxygen quenching capabilities of MOFs could only be achieved when the materials were fully activated by treatment in vacuum and at elevated temperature (0.7 mbar, 120 °C, 72 h). Fig. 3c and d shows the humidity influence on the sensing properties of PCN-224. As can be seen, an increase of relative humidity from 0 to 33% results in some decrease of fluorescence intensity and sensitivity of the material. The behaviour is reversible and the parameters are recovered when dry conditions are established again (Fig. 3c). Increasing relative humidity to 53% results in further decrease of sensitivity (Fig. 3d), again reversible. However, if the humidity is raised to 84%, a drastic decrease of the sensitivity is observed. Comparison of  $K_{SV}$  values at 0 and 84% relative humidity (0.25 kPa<sup>-1</sup> and 0.008 kPa<sup>-1</sup>, respectively) reveals the decrease of sensitivity by about 30-fold. Notably, this effect cannot be reversed by changing back to dry atmosphere but only by activation of the material at elevated temperature and vacuum. The drastic decrease of sensitivity at high humidity may be due to condensation of water inside of the porous channels of the MOF. In this respect substitution of meso-tetracarboxyphenyl porphyrin with (partly) fluorinated analogues may be a promising way to reduce or even completely overcome the above limitation. Porphyrins bearing fluorine atoms in  $\beta$ -position are known,<sup>60</sup> and partial fluorination in the meso-phenyl positions is likely to be feasible.

### Immobilization of MOFs

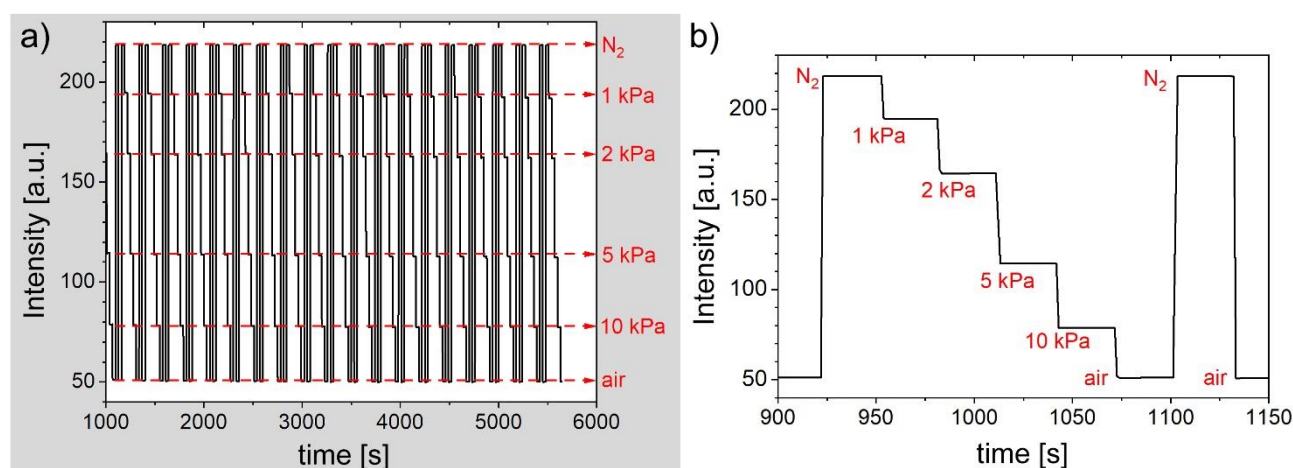
Potential application of MOFs for optical oxygen sensing requires their immobilization into/onto solid supports to obtain a sensing element with acceptable mechanical stability. A notable exception is the application of MOF (micro)crystals in form of aqueous dispersion.<sup>37</sup> For all the experiments, PCN-224 was chosen as the model system but results are expected to be applicable to the metalated congeners due to their high structural similarity. A straightforward way to prepare sensing materials is to disperse crystals in a polymeric matrix. To do so, the free crystals (Fig. 4a) were first dispersed in a polymer solution in an organic solvent that was evaporated after film casting. Hyflon AD 60 was chosen for its high oxygen permeability and chemical inertness.<sup>61</sup> Unfortunately, a drastic loss of sensitivity was observed after immobilization (Fig. 4f).



**Fig. 4.** left: SEM images of the PCN-224 MOF; a) free MOF powder; b) immobilized on electrospun poly(acrylonitrile) nanofibers; c) immobilized on glass fibres of a glass fibre filter; d) crystals grown on silica-gel; e) grown on flat PA filter surface. Right; f) Stern-Volmer plots for PCN-224 immobilized onto/in various matrices.

This may be due to clogging of the pores by flexible polymer chains or entrapped solvent (perfluorodecaline) that hinders oxygen from entering the MOF freely. Notably, perfluorodecaline is much less volatile than water (b.p. 142 °C) and is much larger so it may be very difficult to remove it once it gets entrapped in the pores of the MOF. Moreover, removal of residual solvent from the perfluorinated polymer itself was reported to be challenging.<sup>62</sup>

As an alternative approach, the growth of the MOF on different substrates was investigated.<sup>63</sup> PCN-224 was successfully grown on heat-stabilized poly(acrylonitrile) (PAN) nanofibers (Fig. 4b). PAN nanofibers were prepared via an electrospinning technique and a cross-linking step at high temperature (280 °C) that renders the fibres insoluble in DMF.<sup>64</sup> This property enables the MOF to grow from a solution of the precursors in DMF. SEM revealed MOF crystals grown not only on the surface of the fibres but also around the fibres (Fig. S16) and PXRD confirmed the structure of PCN-224 grown on the fibrous support (Fig. S17). The oxygen sensitivity of the obtained material is very similar to that of the individual crystals (Fig. 4f). This is not the case for several other composite materials. MOF crystals grown on different Si-based materials such as a glass fibre filter (Fig. 4c, Fig. S13) and aluminium-supported silica-gel (Fig. 4d, Fig. S15) exhibited some decrease of oxygen sensitivity (Fig. 4f). The decrease in sensitivity may be due to blocking of some part of the crystals by the virtually oxygen-impermeable glass/silica-gel backbone. PCN-224 was also grown on a flat polyamide (PA) filter (Fig. 6e, Fig. S14) and a similar decrease in the sensitivity was observed (Fig. 4f). For the flat silica-gel and PA supports the individual crystals are comparable in size and the oxygen sensitivity is also very similar.



**Fig. 5.** a) Fluorescence intensity response of PCN-224 grown on PAN nanofibers to alteration of oxygen content in the gas atmosphere during 19 consecutive calibration cycles; b) Dynamic response of PCN-224 grown on PAN nanofibers.

Finally, the sensing properties of PCN-224 grown on PAN nanofibers were investigated in more detail. The response of the material is very fast and fully reversible (Fig. 5a) and is generally similar to that of the free crystals. It should be noted that since the compact PCN-224 crystals are grown around the individual PAN fibres, their position in the sensor material is fixed and there is no possibility of movement of individual crystals anymore. This allows for a very fast exchange of the gas atmosphere so that the measured response times are closer to the true values (in particular when compared to the measurement performed with the free crystals presented in Fig. 4). The full response ( $t_{100}$ ) in both directions was accomplished within 1 s (Fig. 5b), which again appears to reflect the time needed for the gas exchange. The true response times in terms of more commonly used  $t_{95}$  (time needed for 95% of the signal change) are expected to be well below 1 s. During 19 consecutive calibration cycles, almost no drift (less than 2% over a continuous illumination of more than one hour and 19 consecutive cycles) was found and no change in sensing behaviour was observed. Therefore, immobilization by growing PCN-224-related materials on PAN nanofibers can be considered highly promising for preparation of solid state (sensing) materials.

## Conclusions

Porous MOFs prepared from luminescent porphyrins as building blocks show extremely interesting oxygen sensing properties in gas phase. Compared to conventional oxygen-sensing materials it becomes possible to suppress aggregation of dye molecules and achieve high indicator content in the sensing material. High porosity and “free-standing” dye molecules are responsible for unprecedentedly efficient quenching of the luminescence by molecular oxygen. Significant quenching is observed already for the MOF based on a fluorescent porphyrin dye despite its short fluorescence decay time of several nanoseconds. Phosphorescence of MOFs that make use of analogous Pt(II) and Pd(II) porphyrins is quenched by trace amounts of oxygen. The bimolecular quenching constant  $k_q$  is extremely high and exceeds by several folds the value obtained for the porphyrins immobilized in poly(trimethylsilylpropyne), a polymer with the highest oxygen permeability known. MOF growth on porous support materials paves the way for their practical applications in oxygen sensing in gas phase. Among several materials investigated, cross-linked poly(acrylonitrile) nanofibers were found to be particularly promising, since the oxygen-sensing characteristics are virtually the same as for the free crystals. The material shows fast and fully reversible response. A current limitation of the PCN-224 based MOFs in oxygen sensing is the cross-talk to humidity and the drastic decrease of the sensitivity at high humidity. Substitution of the dye molecules used as building blocks by fluorinated porphyrins may help to overcome the current limitation.

## Conflict of interest

The authors have no conflict of interest to declare

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## Supporting Information

The supporting information contains preparations of the precursors, a detailed description of the PXRD experiments and results, SEM images of free crystals and additional SEM images of the immobilized MOFs, PXRD data for PCN-224 grown on PAN-fibres, fit parameters for the Stern-Volmer plots obtained for different samples of PCN-224-based MOFs and Stern-Volmer plots of reference measurements.

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