Supporting Information

Materials and Methods

Pd thin films (60 nm) were deposited at room temperature on quartz substrates in a DC/RF magnetron sputtering system (base pressure 10^{-8} mbar, deposition pressure 0.003 mbar). To ensure better adhesion of the Pd sensing layer on the substrate a 3 nm intermediate Ti layer was sputtered in between. Thickness was determined, with a DekTak3 profilometer.

Microwave-assisted synthesis of the thin film of $Cu(FMA)(Bpe)_{0.5}$ on Pd was prepared by mixing $Cu(NO_3)_2{\cdot}2.5H_2O$ (0.0663 g, 0.285 mmol), H_2FMA (fumaric acid, 0.0331 g, 0.285 mmol), and Bpe (Bpe=trans-bis(4-pyridyl)ethylene, 0.0260 g, 0.143 mmol) in H_2O (25 cm^3) in a Teflon-lined autoclave containing the Pd thin film laid face up, in the bottom. The synthesis was carried out in a microwave oven at a constant 600 W power with a 30 s ramping time followed by a 30 s hold period at the set temperature value (40 °C, 60 °C, 70 °C, 80 °C and 100 °C, temperature was monitored in the solution phase) to optimise the reaction temperature. In addition, since the 70 °C yielded the best surface coverage of MOF particles yet caused no damage to the Pd film, the reaction time was also optimised by using hold periods of 30 s, 60 s, 5 min, 10 min and 20 min, the best result was obtained with 10 min heating as after 20 min the Pd film showed signs of cracking.

Solvent exchange and dissolution of unreacted reactants trapped in the pores and on the surface of the MOF thin film were carried out overnight at ambient temperature in excess ethanol. Activation of samples was performed in vacuum at 100 °C, overnight.

Diffuse Reflectance Infra-Red Fourier Transform spectra (DRIFTS) were recorded on a Nicolet 8700 model spectrometer, equipped with a high-temperature cell, and a deuterated triglycine sulfate and thermoelectricity cooled (DTGS-TEC) detector. The spectra were acquired with 256 scans at 4 cm^{-1} resolution from 4000 to 500 cm^{-1} using the pristine Pd thin film to perform background experiments. The samples were pre-treated at 453 K for 1 hour in a helium flow of 20 cm^3 min^{-1}.

Powder X-Ray Diffraction data was collected using Bruker D8 Advance X-ray diffractometer (Co-K_α, λ=0.178897 nm) equipped with a LynxEye detector in the Bragg-Brentano configuration.

The morphology and chemical composition of thin films were investigated with Scanning Electron Microscopy Energy-Dispersive X-Ray Spectroscopy (SEM-EDS, JEOL JSM-6010LA instrument equipped with a tungsten hairpin filament and an energy dispersive X-ray microanalyser). Samples were investigated in the secondary electron imaging mode (SEI), using an Everhart-Thornley type detector. SEM images were collected using the accelerating voltage of 5 kV. The X-ray spectra were recorded with an energy dispersive spectrometer equipped with a silicon-drift detector, using the accelerating voltage of 20 kV.

A flow setup in reflection mode was used to characterise the optical response of thin films. A controlled flow of 200 cm^3 min^{-1} Ar carrier gas was applied while three mass flow controllers regulated hydrogen and carbon monoxide amounts in the feed flow. For safety, H_2 and CO levels concentrations were kept low. The outlet of the flow cell was connected to a wash bottle filled with oil to prevent backflow. A multimode optical fibre was used to guide the light of a tungsten-halogen light source towards the Pd thin film. An Ocean Optics USB4000 spectrometer was used to measure the optical-signal change in the entire wavelength range from UV to near infrared, mainly data at 635 nm, corresponding to the wavelength at which low cost LEDs and photodiodes operate, is shown. Measurements are averaged over 10 data points.

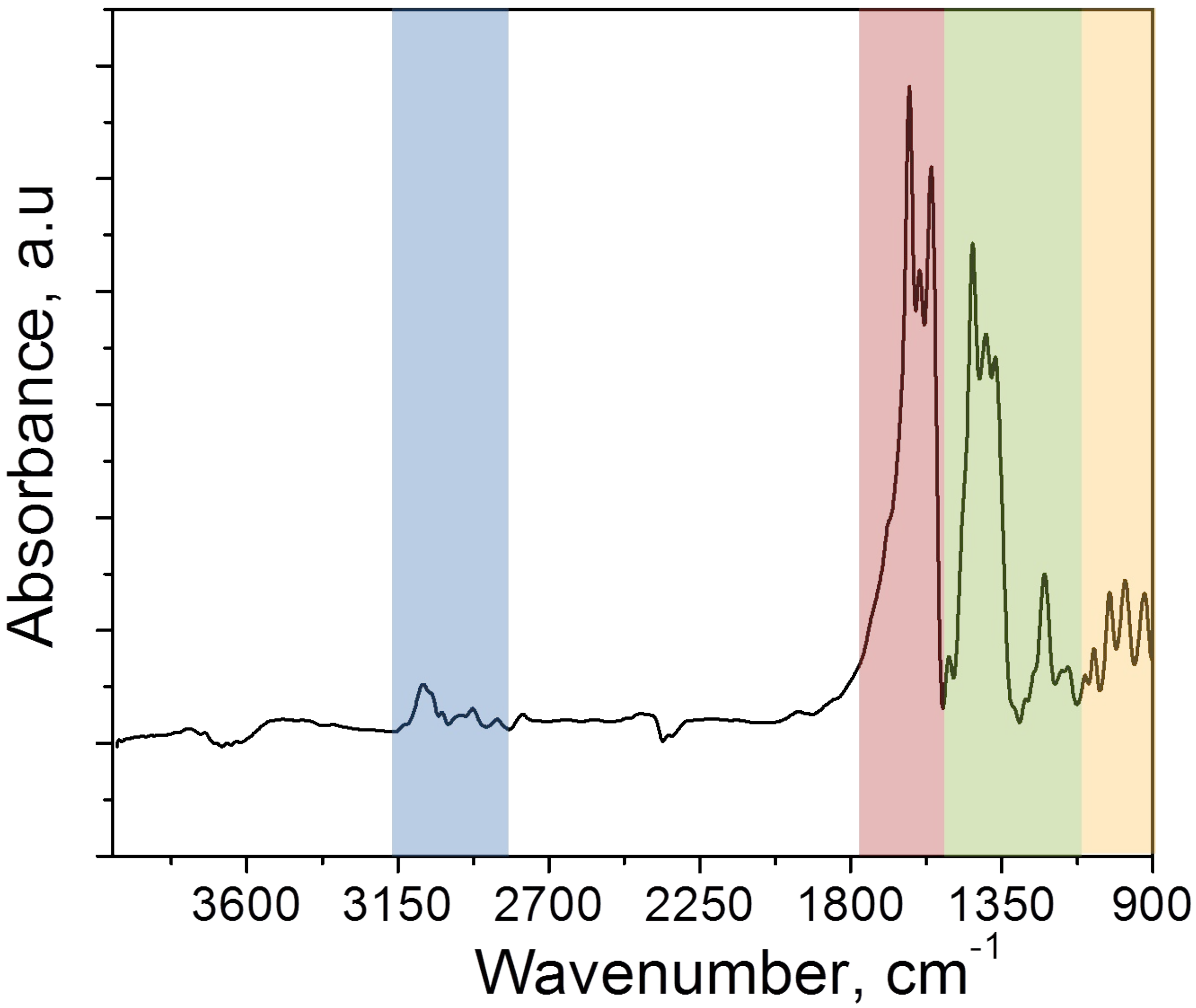

Figure S1. Representative DRIFT spectrum of Cu(FMA)(Bpe)$_{0.5}$-coated Pd specimen, indicating some group frequency regions highlighted as follows, in blue: C(Ar)-H and =C-H stretch; in red: C(Ar)-C(Ar) and C(Ar)-N ring, C=C stretch and -CO$_2$ asymmetric stretch modes; in green: C(Ar)-C(Ar) and C(Ar)-N ring, C(Ar)-H and =C-H deformation and -CO$_2$ symmetric stretch modes and in yellow: C(Ar)-C(Ar) and C(Ar)-N ring, C-C rock and =C-H in-plane and out-of-plane modes.

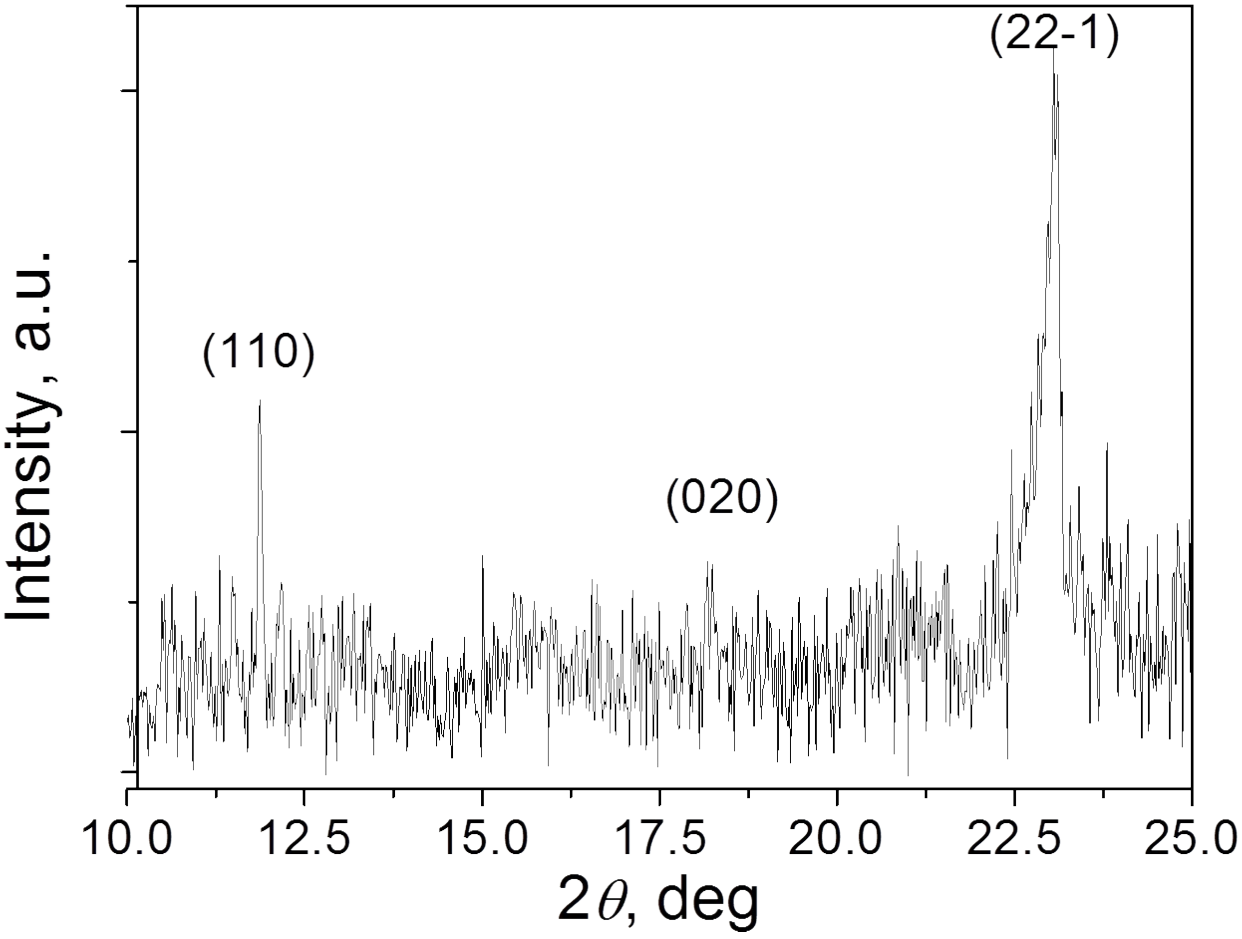

Figure S2. X-ray diffraction pattern of a selected Cu(FMA)(Bpe)$_{0.5}$-coated Pd specimen indicating a number of discernible diffraction peaks.

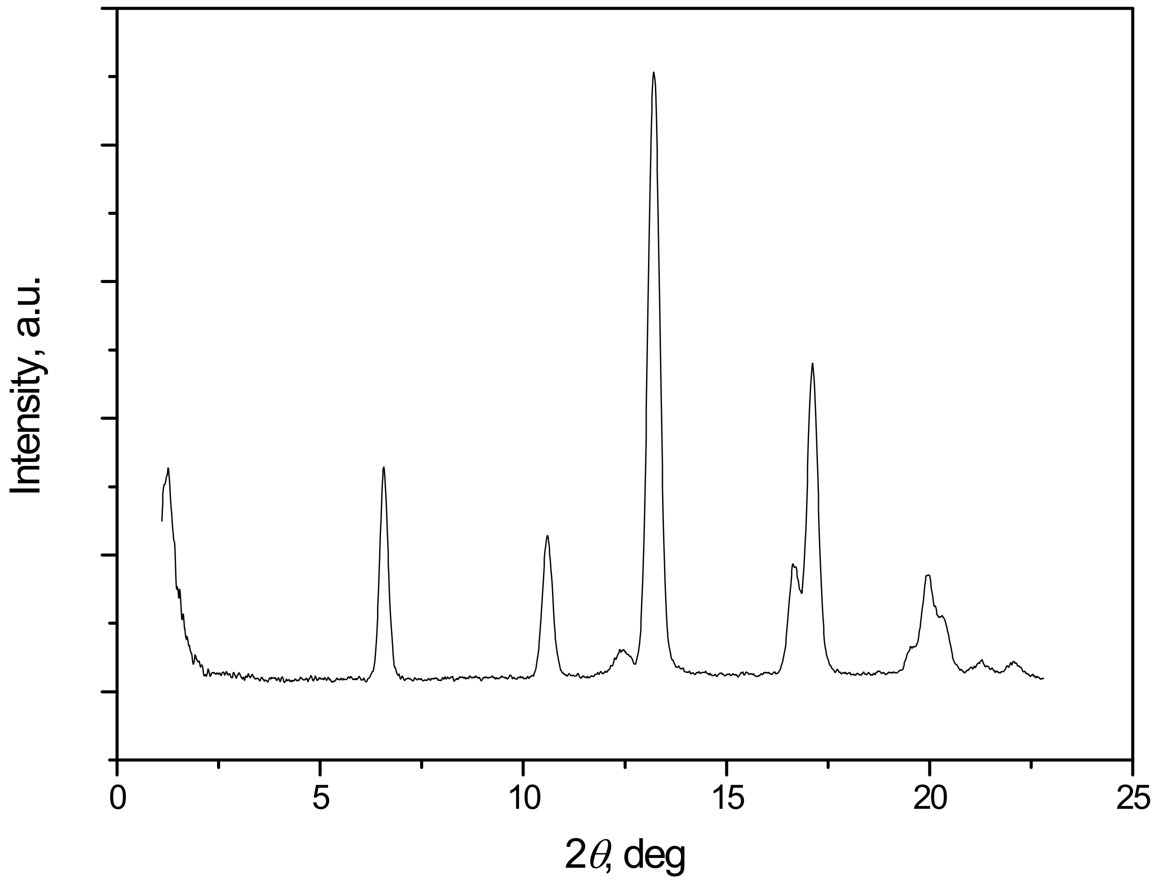

Figure S3. X-ray diffraction pattern of bulk Cu(FMA)$(Bpe)_{0.5}$.

Discrepancies in diffraction peak positions may arise from the interaction of the thin MOF layer with the substrate and/or from the inhomogeneousness of the thin-film sample surface when data is collected in the Bragg-Brentano configuration.

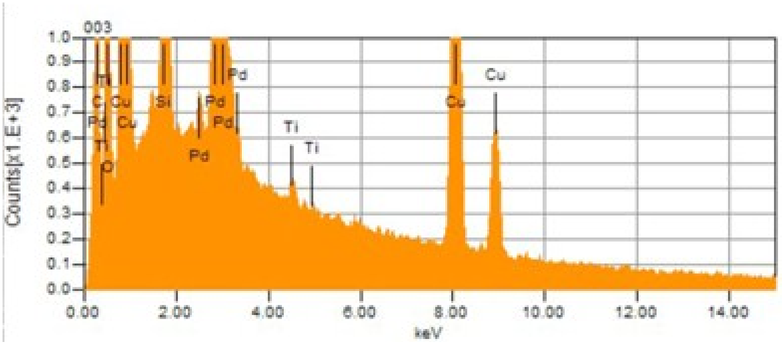

Figure S4. EDS spectrum of a selected Cu(FMA)$(Bpe)_{0.5}$-coated Pd specimen.