Chemical Communications

SUPPLEMENTARY INFORMATION

Ion Flow in Zeolitic Imidazolium Framework Results in Ionic Diode Phenomena

Elena Madrid,[a] Mark A. Buckingham,[a] James M. Stone,[b] Adrian T. Rogers,[c] William J. Gee,[a] Andrew D. Burrows,[a] Paul R. Raithby,[a] Veronica Celorrio,[d] David J. Fermin,[d] and Frank Marken*[a]

Supplementary data are provided for

- Raman analysis of bulk-grown and pore-grown ZIF-8 materials (Figure SI1)
- XRD data comparing bulk-grown ZIF-8 and eosin Y stained ZIF-8 (Figure SI2)
- Impedance data comparing an open pore with a ZIF-8-filled pore in aqueous $NaNO_3$ (Figure SI3)
- Cyclic voltammetry data for a 24h-grown ZIF-8-filled pore immersed in 10 mM NaOH | 10 mM HCl showing the first 5 potential cycles.

Figure SI1 shows Raman data comparing ZIF-8 prepared in solution and ZIF-8 grown in the PET hole. Raman scattering measurements were performed at room temperature in the backscattering geometry using a RENISHAW inVia Raman microscope equipped with a CCD camera and a Leica microscope. A Renishaw HPNIR 785 nm diode laser with a max power of 180 mW was used as an excitation source. Prior experimental analysis, the 520.5 cm^{-1} band of a silicon wafer is used to calibrate the instrument. Powder samples were mounted on a glass slide and the spectra were taken using a 5× objective. During measurements the laser power was reduced to 50% using a transmission filter in order to avoid sample damage. For each spectrum a laser exposure time of 20 s was selected and ten scans were accumulated between 3200 and 200 cm^{-1} with a resolution of approx. 1–2 cm^{-1}. The data were collected and analysed with Renishaw Wire and Origin Pro8 software.

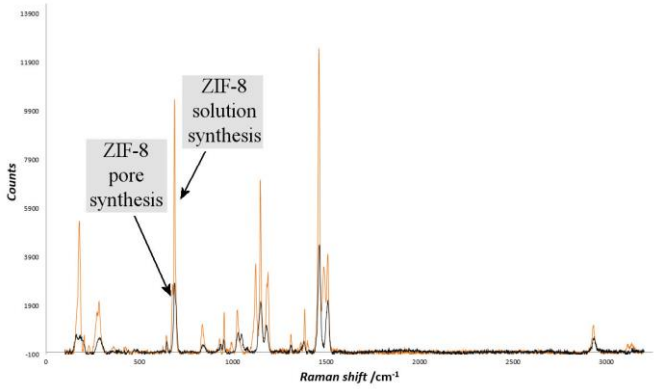

Figure SI1. Raman data (785 nm) for ZIF-8 synthesised in solution and ZIF-8 synthesised directly in the PET hole.

Figure SI2 shows a photograph of ZIF-8 powder as synthesised and after it has been stained with eosin Y (by immersion in 50:50 water: ethanol containing 0.1 mM eosin Y). Figure SI2 also shows PXRD data comparing ZIF-8 and eosin Y stained ZIF-8 (measurements of the samples were carried out on a Bruker AXS D8 Advance X-ray diffractometer with Cu Kα radiation (λ = 1.542 Å) in the 2θ range of 4–60°; step size was 0.02° with time per step of 1.00s; The reference ZIF-8 PXRD spectrum was calculated using single crystal data with the software LAZY PULVERIX by K. Yvon, W. Jeitschko, E. Parthé, *J. Appl. Cryst.*, **1977**, *10*, 73-74).

[a] *Department of Chemistry, University of Bath, Bath BA2 7AY, UK, Email F.Marken@bath.ac.uk*
[b] *Centre for Photonics and Photonic Materials, Department of Physics, University of Bath, Bath BA2 7AY, UK*
[c] *Address here. Microscopy and Analysis Suite, Department of Physics, University of Bath, Bath BA2 7AY, UK*
[d] *School of Chemistry, University of Bristol, Bristol, BS8 1TS, UK*

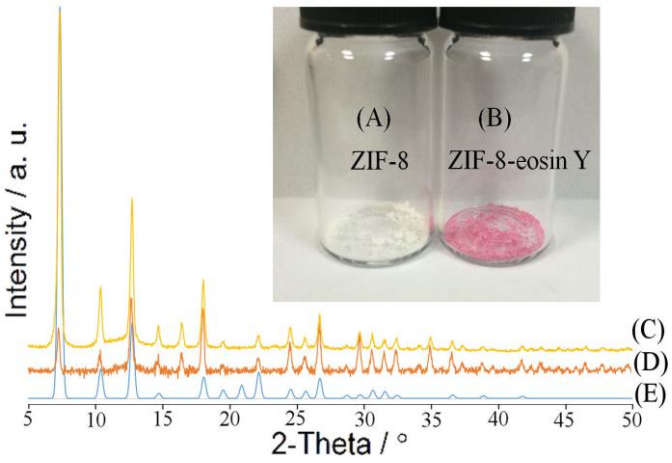

Figure SI2. (A,B) Photograph with ZIF-8 powder and eosin Y stained ZIF-8 powder material. (E) Calculated ZIF-8 XRD data compared to experimental XRD data for (C) ZIF-8 and (D) eosin Y stained ZIF-8.

In XRD data, the as-synthesised ZIF-8 matches the pattern for the predicted ZIF-8 but for an additional peak at 2Θ of *ca* 16, which corresponds to a reflection of order for ZIF-8 corresponding to the (310) plane. This peak, as well as an the additional peaks at *ca* 35, are evident in other reports of aqueously synthesised ZIF-8 {a) K. Kida, M. Okita, K. Fujita, S. Tanaka and Y. Miyake, *CrystEngComm*, 2013, **15**, 1794, b) Meipeng Jian, Bao Liu, Ruiping Liu, Jiuhui Qu, Huanting Wang and Xiwang Zhang, *RSC Adv.*, 2015, **5**, 48433}, and are likely a result of these growth conditions favouring certain crystalline morphologies

Figure SI3 shows impedance data comparing an open 20 μm diameter hole in PET with a ZIF-8-filled hole. Experiments have been carried out in 4-electrode configuration and with aqueous 1 mM $NaNO_3$ in both sides of the electrochemical cell.

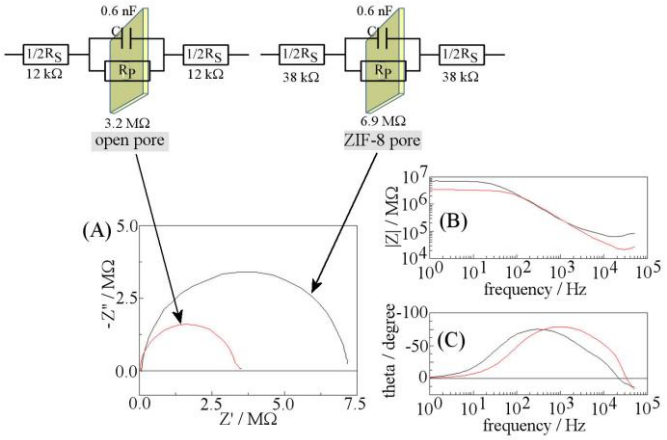

Figure SI3. Impedance data (4-electrode, open circuit, 25 mV amplitude, 1 to 10^5 Hz) for a 24h growth ZIF-8-filled hole compared to an open 20 μm diameter hole in PET. Shown are (A) Nyquist plot and (B,C) Bode plots obtained in 1 mM $NaNO_3$ | 1 mM $NaNO_3$.

Figure SI4 shows consecutive cyclic voltammograms for a ZIF-8-filled hole in PET immersed on one side in 10 mM NaOH and on the other side in 10 mM HNO_3.The dashed line indicates the current for the open hole under the same conditions.

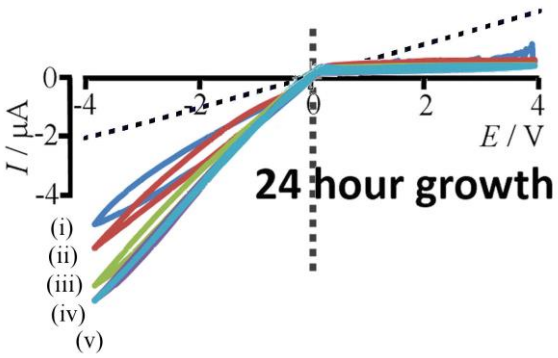

Figure SI4. Cyclic voltammograms (5 cycles shown as (i) to (v), 24 h growth, scan rate 20 mV s^{-1}) in 10 mM NaOH | 10 mM HNO_3 comparing an open pore (dashed potential between +/-4 V) with a ZIF-8-filled pore. The voltammogram reaches a steady state.