

## *Electronic Supplementary Information*

Why conductivity is not always king – physical properties governing the capacitance of 2-D Metal-Organic Framework - based EDLC supercapacitor electrodes: Ni<sub>3</sub>(HITP)<sub>2</sub> as a case study

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### **Experimental**

#### **Starting materials**

Nickel chloride hexahydrate (NiCl<sub>2</sub>·6 H<sub>2</sub>O) was purchased from ACROS and used without further purification. Deionised water from a Millipore system was used as the solvent and 2,3,6,7,10,11-hexaaminotriphenylene hexahydrochloride (HATP·6 HCl) was prepared according to a procedure described elsewhere [1]. For preparing the HATP·6 HCl, the starting materials were purchased from Sigma-Aldrich or TCI and were used without further purification unless otherwise noted. Tris(dibenzylideneacetone)dipalladium(0), Pd<sub>2</sub>(dba)<sub>3</sub>, was purchased from Oakwood Products (Fluorochem). Hexane, diethyl ether, ethyl acetate, toluene and silica gel were purchased from VWR. THF and toluene were collected from an alumina column solvent purification system.

#### **MOF synthesis**

The general standard synthesis is obtained through a solvothermal reaction of 2,3,6,7,10,11-hexaaminotriphenylene hexahydrochloride (HATP·6 HCl) with nickel chloride hexahydrate (NiCl<sub>2</sub>·6 H<sub>2</sub>O) in a 2:3 molar ratio, in an aqueous solution under air at 60 °C, with the addition of base. For HITP\_A the base used was sodium acetate, CH<sub>3</sub>COONa, the reaction was performed in a 250 ml round bottom flask that was bubbled with air for 45 minutes and subsequently bubbled with nitrogen for 1.5 hours. For HITP\_B, the base used was 14 M ammonia, NH<sub>4</sub>OH, the reaction was performed in an open 250 ml beaker and was bubbled with air for 2 hours. For HITP\_C the reaction was the same as for the HITP\_B, except on a smaller scale with a 50 ml beaker used. The resulting black powders were centrifuged and washed in water and subsequently in ethanol, after which were dried on the Schlenk line. The drying times for the subsequent batches were respectively 2 h, 2h and 20 h.

#### **Characterization**

Powder X-ray diffraction (PXRD) was taken of the dry powders using a Bruker D8 Advance diffractometer in a  $\theta/2\theta$  Bragg-Brentano geometry, with a Cu K $\alpha$  anode ( $\lambda = 1.5405 \text{ \AA}$ ) and the powder was placed on a zero-background silicon (510) plate on the sample stage. The N<sub>2</sub> isotherms were taken at 77 K and the CO<sub>2</sub> isotherms at 298 K, using a Micrometrics ASAP 2020 and the BET theory was applied to calculate the internal surface area (see Figures S2-S4). Scanning electron microscopy (SEM) was performed using a Zeiss Supra 55Vp FEG SEM with an operating voltage of 14 kV using an in-lens secondary electron detector. The materials were stable under electron-beam irradiation during imaging.

#### **Electrode preparation**

The electrodes for electrochemical testing were prepared using neat MOF materials, at 5 mg from each batch. That material was pressed into Ni foams to form a mechanically stable electrode. An Ag/AgCl wire was made by dipping an Ag wire in Clorox for 10 minutes and used as a pseudo reference electrode while the counter electrode was prepared using a mixture of 90:5:5 mass percentages of activated carbon, conducting carbon black and PVDF binder. The total mass of the counter electrode was 50 mg to account to be able to balance the charge on the working MOF electrode. The 3 electrode cells were prepared using a stainless steel body published elsewhere [2] and two trilayer polypropylene/ polyethylene/ polypropylene Celgard C480 separators and the electrolyte used was 1 M KOH in water. A Biologic SP 200 potentiostat was used for the electrochemical tests. The cyclic voltamperometry scans were taken with voltage sweep rates from 1 V·s<sup>-1</sup> to 1 mV·s<sup>-1</sup> and the specific capacitance  $C_g$  was calculated from CV plots using the equation

$$C_g = \frac{\int_{U_{min}}^{U_{max}} I(U) dU}{2m(U_{max} - U_{min})v}$$

, where  $m$  – mass of the electrode,  $U_{max}$  and  $U_{min}$  are the maximum and minimum voltages of the test voltage range,  $I(U)$  is the current as a function of the voltage and  $v$  is the voltage sweep rate. The minimum and maximum voltages were determined to be respectively -0.6 and -0.1 V vs Ag/AgCl in the used configuration. Electrochemical impedance spectra (EIS) were measured for all cells at the initial open circuit voltage in the range 1 MHz to 10 mHz using a 10 mV sine wave and the analyses of the EIS were done using the EC-Lab software using an equivalent circuit consisting of an ESR in series with parallel connected charge transfer constant phase element and a charge-transfer resistor with a diffusion constant phase element.

## References

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Sheberla, D.; Bachman, J. C.; Elias, J. S.; Sun, C.-J.; Shao-Horn Y.; Dincă, M. Conductive MOF Electrodes for Stable Supercapacitors with High Areal Capacitance. *Nat. Mater.* **2017**, 16, 220–224.

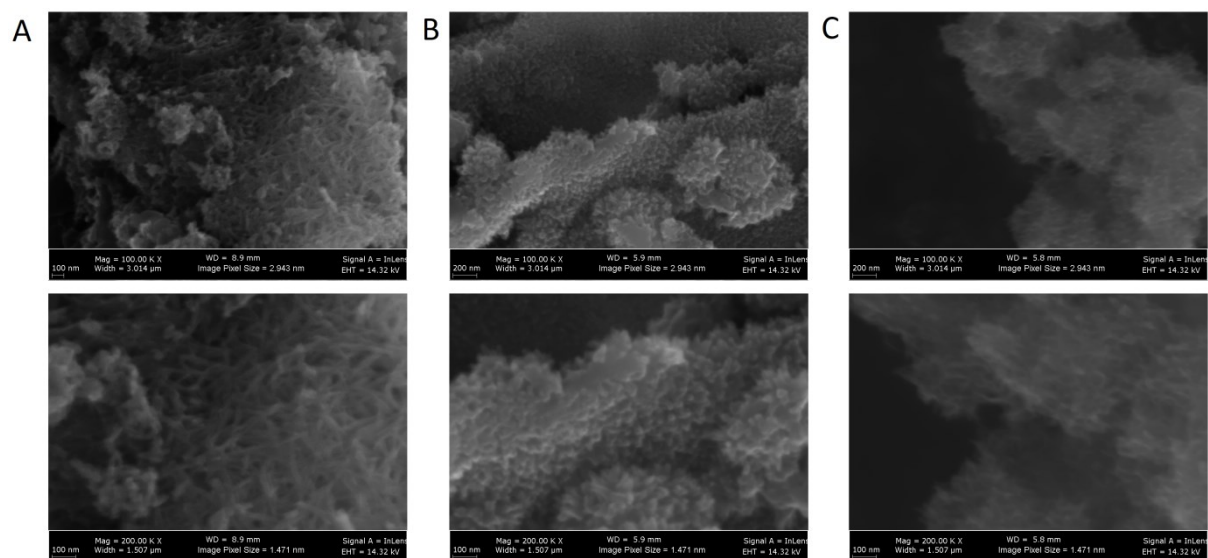


Fig. S1. SEM images of the NiHITP\_A (column A), NiHITP\_B (column B) and NiHITP\_C (column C).

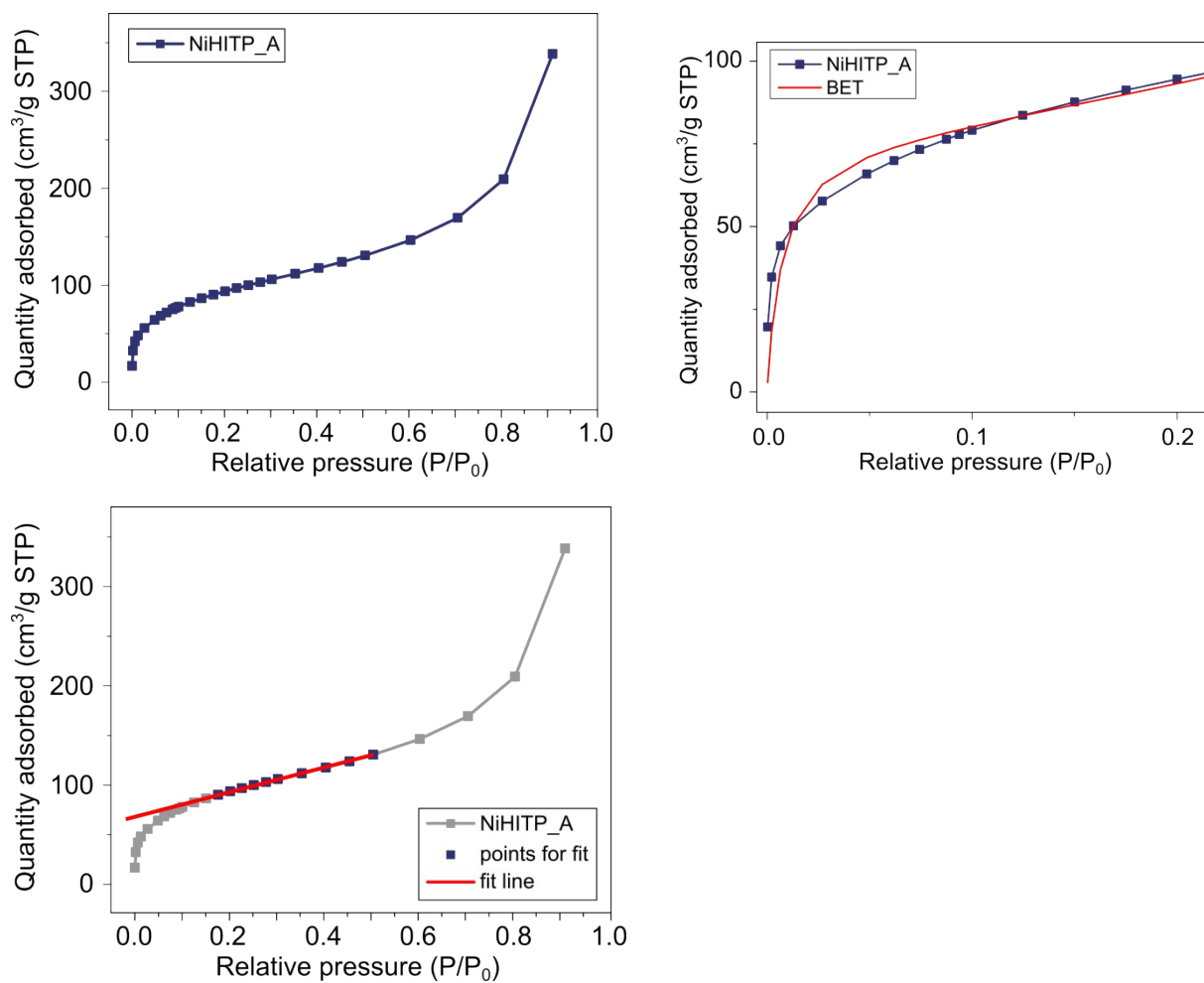


Fig. S2. N<sub>2</sub> adsorption isotherm plot for NiHITP\_A with BET fit (right) and t-fit (bottom).

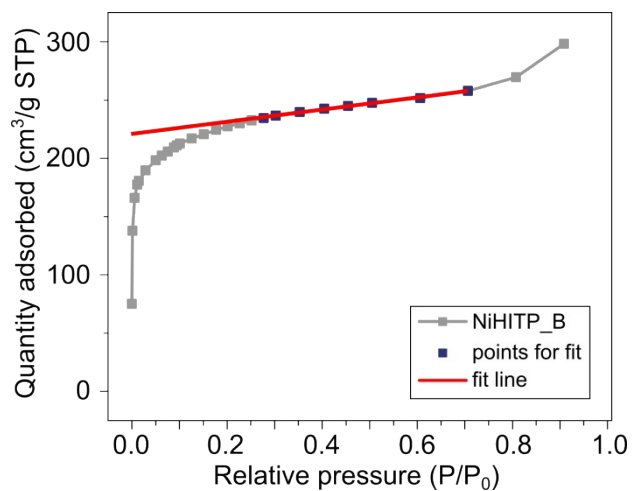
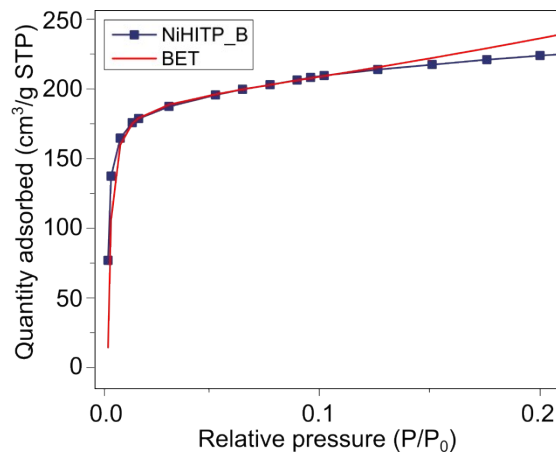
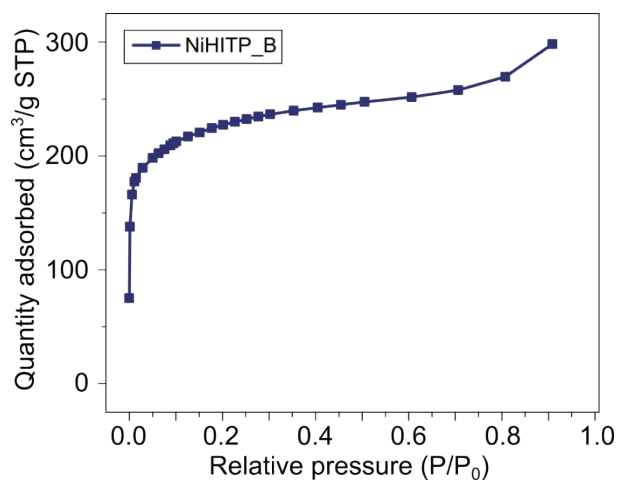


Fig. S3. N<sub>2</sub> adsorption isotherm plot for NiHITP\_B with BET fit (right) and t-fit (bottom).

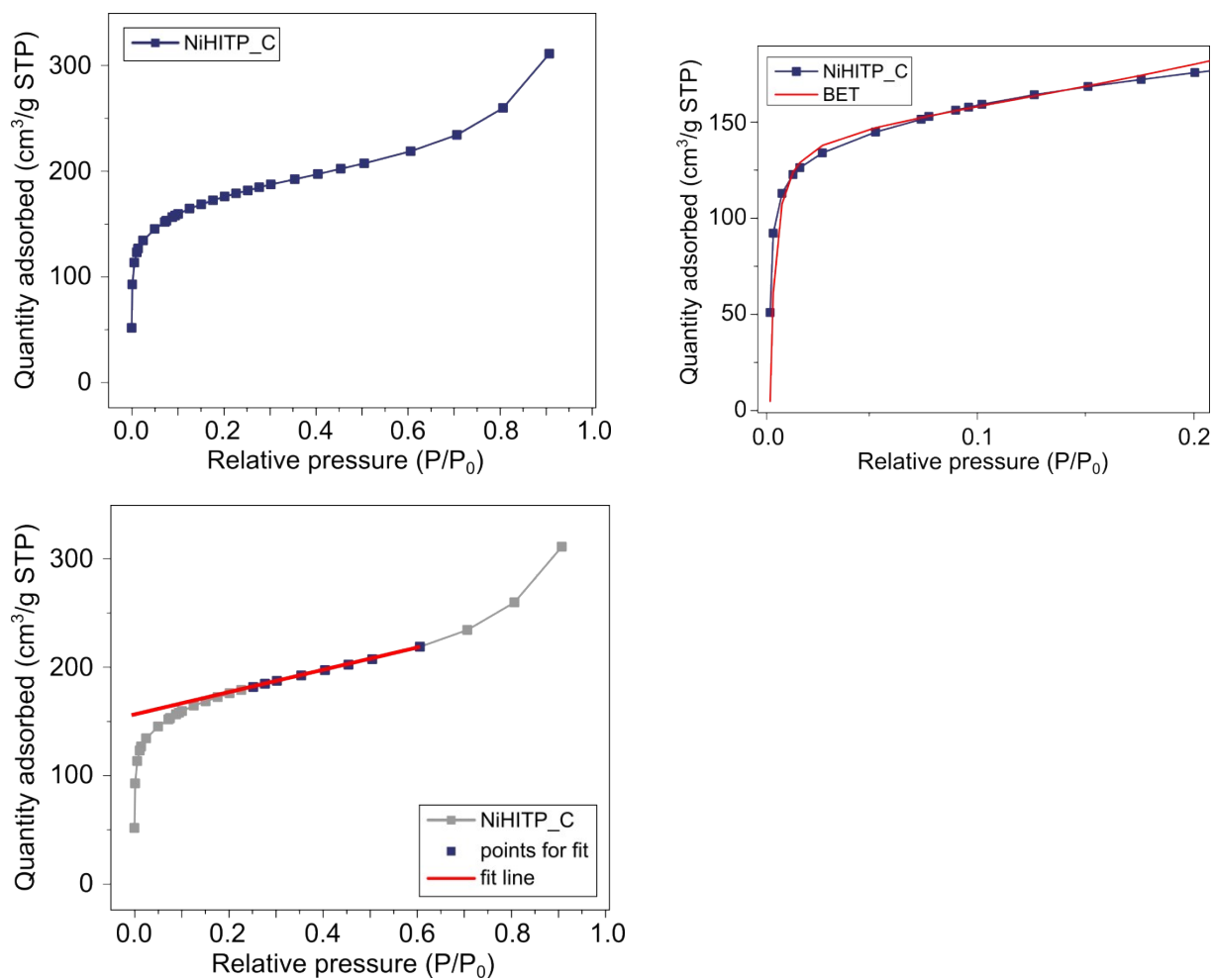


Fig. S4. N<sub>2</sub> adsorption isotherm plot for NiHITP\_C with BET fit (right) and t-fit (bottom).