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Molecular understanding of charge storage and charging dynamics in supercapacitors with MOF electrodes and ionic liquid electrolytes

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Abstract

We performed constant-potential molecular dynamics simulations to analyze the double layer structure and capacitive performance of supercapacitors composed of conductive metal–organic framework (MOF) electrodes and ionic liquids. The molecular modeling unravels how ions transport and reside inside polarized porous MOFs, and then predicts the corresponding potential-dependent capacitance in characteristic shapes. Transmission line model was adopted to characterize the charging dynamics, which further allowed evaluating the capacitive performance of this class of supercapacitors at macroscale from the simulation-obtained data at nanoscale. These ‘computational microscopy’ results were testified by macroscopic electrochemical measurements. Such combined nanoscale-to-macroscale investigation demonstrates the potential of MOF supercapacitors for achieving unprecedentedly high volumetric energy and power densities. It gives molecular insights into preferred structures of MOFs for accomplishing consistent performance with optimal energy–power balance, providing a blueprint for future characterization and design of these new supercapacitor systems.

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23 Enhancing capacitive performance of electrical **double layer capacitors** (EDLCs) relies on the
24 development of porous electrode materials.^{1,2} Owing to their designable structures,^{3,4,5}
25 conductive **metal-organic frameworks** (MOFs) are promising for EDLC electrodes.^{5,6,7,8} Their
26 scaffold-shaped volume-filling ordered structure could bring large **specific surface area** (SSA)
27 per mass/volume, with a custom-designed pore space.^{3,6} This helps to maximize the stored
28 energy density; it may also facilitate ion transport, thereby increasing power density. Indeed,
29 graphene-doped MOFs were found to give high capacitance, due to their high porosity and open
30 structure.⁹ Highly conductive Ni₃(2,3,6,7,10,11-hexaiminotriphenylene)₂ (Ni₃(HITP)₂) MOF-
31 electrodes in EDLCs with an organic electrolyte showed high areal capacitance and low cell
32 resistance, superior to most carbon-based materials.¹⁰

33 The choice of electrolyte is equally important. **Room temperature ionic liquids** (RTILs) are
34 promising electrolytes due to their excellent thermal stability, nonvolatility, broad working
35 temperature range, and wide electrochemical window (potentially facilitating the EDLC's energy
36 density).^{11,12,13,14} Many studies focused on understanding the energy-storage mechanism of
37 porous electrodes with RTILs, via *in situ* experiments and molecular simulations.^{11,15,16,17,18}
38 Traditional electrodes, e.g. activated carbons, contain pores of different sizes, shapes, and
39 connectivities,^{1,2,3} whereas MOFs present monodisperse pores of controllable structures,^{3,4,5,7}
40 making them near-ideal systems for computational modeling. Nevertheless, because there could
41 be millions of MOF-RTIL combinations, it is important to unravel generic charge-storage
42 mechanisms and charging dynamics related to their structures, particularly in the absence of
43 experimental studies on supercapacitors with conductive MOF-electrodes and RTIL-electrolytes.

44 Herein, we focus on this task, using ‘computational microscopy’: **molecular dynamics** (MD)
45 simulations based on atomistic models of MOFs and coarse-grained models of RTILs and
46 connecting with ‘experimental macroscopy’: electrochemical measurements on MOF-RTIL
47 supercapacitors. Fig. 1a shows our MD setup; we consider three types of electrodes based on
48 densely stacked 2D-conductive MOF-sheets with different-sized quasi-1D pores (Fig. 1b-c), and
49 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF₄]) as the electrolyte (Fig. 1d). In
50 simulations, we control the voltage between cathode and anode by constant potential method.
51 Details see Methods and Supplementary Parts 1-2. After equilibrating the system at the
52 potentials of **zero charge** (PZC), we apply jump-wise voltages between two electrodes, and then

53 monitor the follow-up charging dynamics and charge/ion distributions. We explore structures of
54 ionic distributions in electrically polarized nanoscale pores, and the options for energy storage
55 and power delivery that these structures proffer. Finally, we experimentally test the simulation-
56 predicted performance.

57 **Equilibrium charge and ion distributions inside MOFs**

58 We present the simulated charge and ion distributions in three neutral and polarized MOFs in
59 pore sizes of 0.81, 1.57 and 2.39 nm, with PZC calculated as 0.074, 0.035 and 0.042 V,
60 respectively. The small PZC values suggest that no noticeable preferential adsorption of cations
61 or anions of [EMIM][BF₄] into the pores of these MOFs.¹⁹

62 Figure 2a depicts the in-plane distributions in a 1.57-nm-diameter pore at different electrode
63 potentials. Inside quasi-1D pores of a polarized MOF-electrode, radial ion distributions appear
64 more heterogeneous than those at PZC, with counter-charge settling closer to the pore surface
65 and at pore center-line (up row of Fig. 2a). At PZC, as shown in the middle and bottom rows of
66 Fig. 2a, cations and anions both form a layer adsorbed on the pore surface, displaying a
67 hexagonal pattern in the planar-cross-section, with a wire of ions along the pore axis. Under
68 electrode polarization, the *counter-ions* (cations at negative and anions at positive polarization)
69 pack similarly but with more distinct separation between a surface-adsorbed layer and the center-
70 line. The *co-ions* settle between these two regions. For the smallest pore MOF (0.81 nm), only
71 one layer of ions can get inside the pore, regardless of electrode polarization (Supplementary
72 Figure 5). For the largest pore (2.39 nm), at PZC, two mixed cation-anion layers dwell inside the
73 pore, one of them contacting pore wall; with electrode polarization two pronounced counter-ion
74 layers form separated by a co-ion layer, with a co-ion wire at the axis (Supplementary Figure 6).

75 The interlaced radial distributions of cations and anions in polarized pores comply with the
76 ion layering in RTILs at electrode surfaces revealed by previous experiments and simulations,^{11,}
77 ^{15, 16, 17} while there is little cation-anion layering at PZC (middle column of Fig. 2a). To delve
78 into this difference, we analyzed the ion density along the pore axis. In Supplementary Figure 7a
79 we see waving axial ion distributions at PZC become more distinct with electrode polarization.
80 Examining ions inside pores, we divided the pore space into central and surface regions
81 demarcated by a circle (Fig. 2b and snapshots in Supplementary Figure 7b). The cation
82 orientations, characterized by angular distributions (Fig. 2c), reveal how ions get accommodated

83 inside the pore. As the electrode gets more negatively charged, cations in the surface region
84 prefer to align along the pore axis, while those in the central region orient more randomly, which
85 could be ascribed to the adsorbed ion layer screening out the electrode surface charge. With
86 positive polarization, the cations move closer to the center-axis and leave their ethyl groups
87 pointing to surface-adsorbed anions. Similar trends could be observed for smaller and larger
88 pores (Supplementary Figures 8 and 9), except that ions in the central region of larger pores
89 orientate more randomly. The delineated in-plane and axial ion distributions unravel where and
90 why ions could preferably reside in MOF-pores.^{11, 15, 20}

91 **Capacitance and energy density of MOF-based supercapacitors**

92 Charge storage in supercapacitors is characterized by voltage-dependent capacitance and energy
93 density. Differential capacitance of an electrode is defined as the derivative of the electrode's
94 charge with respect to its potential (Methods and Supplementary Part 2). The electrode charge is
95 equal with an opposite sign to the net ionic charge inside the pores and in the double layer at the
96 electrode's outer surface. For highly porous electrodes, the area of the latter is negligible, and we
97 will not consider that contribution.

98 The capacitance is usually presented per unit (i) surface area (*area-specific*), (ii) mass
99 (*gravimetric*), or (iii) volume (*volumetric*) of the electrode. The gravimetric and volumetric
100 values are easy to define, whereas the determination of the area-specific capacitance could be
101 ambiguous, as it depends how the interior surface of the electrode was measured (the way how
102 we estimated 'surface area' of the studied MOF-pores is described in Supplementary Part 1). Fig.
103 3a shows the area-specific differential capacitance. The MOF with the smallest pore (0.81 nm)
104 displays a camel-like shape of the capacitance-potential curve with two maxima of 10.2 and 8.8
105 $\mu\text{F cm}^{-2}$ at -1.1 and +1.5 V, respectively, while the curves for the other two MOFs are both bell-
106 shaped with a maximum near PZC. Within a potential range of -0.5 to +0.5 V, the 1.57-nm-
107 diameter MOF delivers a capacitance of $\sim 9 \mu\text{F cm}^{-2}$, compatible with RTIL-based porous carbon
108 EDLCs.^{17, 21} The shape of the capacitance-potential curves could be understood through
109 analyzing the voltage-dependent ion distributions inside pores (Supplementary Figure 10). There,
110 for the smallest pore MOF, the number of in-pore cations and anions, separately, gradually
111 changes within the potential range between -1 and +1.4 V (Supplementary Figure 10a). The
112 change gets faster under larger electrode polarizations, slowing down after ± 2 V, approaching

113 saturation. This results in the camel-like shape of capacitance-potential curve (Fig. 3a). For the
114 other two MOFs (Supplementary Figure 10b-c), the steepest change in ion population occurs
115 near PZC, slowing down as electrodes get more polarized (especially, over ± 1.5 V); this induces
116 bell-shaped capacitance-potential curves (Fig. 3a). Notably, for pores filled with more than one
117 ion layer, within the potential range of -0.5 to +0.5 V the change of cation/anion population takes
118 place majorly in the central region of a pore, but it shifts towards the pore surface region beyond
119 this range (Supplementary Figure 10d-e).

120 Having defined the mass and volume of a unit cell for the studied MOFs, we obtain the
121 gravimetric/volumetric capacitances, and the corresponding energy densities. As shown in Fig.
122 3b-c, the MOF with the largest pore (2.39 nm) has the highest gravimetric capacitance but lowest
123 volumetric one. For 1.57-nm MOF $\text{Ni}_3(\text{HHB})_2$, the gravimetric and volumetric capacitances
124 reach 112 F g^{-1} and 105 F cm^{-3} , respectively. Noteworthy, simulations show that a gravimetric
125 energy density of $\sim 57 \text{ Wh kg}^{-1}$ could be achieved at a cell voltage of 4 V, if the electrodes could
126 sustain this voltage. Such energy density is as high as those reported for some high-energy-
127 density carbon electrodes.²² With regards to volumetric energy density, especially within a
128 narrower potential range, three MOF electrodes display similar capacitances, while at 4 V, the
129 smallest pore MOF delivers the highest volumetric energy density, $\sim 50 \text{ Wh L}^{-1}$. The predicted
130 volumetric performance demonstrates promising potential of these MOFs in comparison with
131 other electrode materials in EDLCs.^{23, 24}

132 Certainly, as the pore size of MOFs keeps reducing, ions eventually will not be able to enter
133 the pores, leading to vanishing capacitance. Indeed, MOF $\text{Ni}_3(\text{hexaaminobenzene})_2$
134 ($\text{Ni}_3(\text{HAB})_2$),⁸ with quite less room than $\text{Ni}_3(\text{HHB})_2$ to accommodate enough ions inside, was
135 explored to exhibit considerably smaller capacitance, suggesting that there would be a limit of
136 narrowing MOF pore for a typical RTIL (Supplementary Part 4).

137 **Charging dynamics**

138 We focus now on power delivery. Figure 4a shows the time evolution of ionic charge in a pore at
139 400 K (for results between 300 to 400 K, see Supplementary Figure 13). It appears possible to
140 rationalize the charging dynamics through the transmission line model (TLM).²⁵ Based on TLM
141 schematized in Supplementary Figure 14a, the net charge of the pore, after jump-wise applying a
142 constant potential, reads:²⁵

$$143 \quad Q(t) = Q_{\infty} \left\{ 1 - \frac{2}{\pi^2} \sum_{n=0}^{\infty} \frac{\exp\left[-\pi^2 \left(n + \frac{1}{2}\right)^2 \left(\frac{2l}{L}\right)^2 \frac{t}{\tau}\right]}{\left(n + \frac{1}{2}\right)^2} \right\} \quad (1)$$

144 where Q_{∞} is the charge when the pore gets fully charged, l is the pore volume divided by its
 145 surface area, and L is the full length of the pore. The parameter in Eq. (1), which does not depend
 146 on pore length, is the intrinsic relaxation time,

$$147 \quad \tau = \frac{C_{area} \times l}{\sigma} \quad (2)$$

148 in which C_{area} is the areal capacitance of the pore and σ is the ionic conductivity inside the pore.
 149 Note that Eq. (1) is strictly valid for potential-independent capacitance; there is no closed-form
 150 solution if the capacitance varies during charging. For simplicity, we will still use Eqs. (1) and (2)
 151 with the value of C_{area} corresponding to the capacitance for a given electrode potential.

152 Taking 1.57-nm-diameter MOF, with $l = 0.40$ nm and $L = 5.86$ nm (parameters for the other
 153 two MOFs, see Supplementary Tables 2-3), by fitting TLM to simulation data we obtain τ .
 154 Despite the aforementioned approximation, TLM-fitted curves match the MD-obtained charging
 155 curves very well (see Fig. 4a). This is further confirmed by fittings of the charging dynamics
 156 under alternative voltage-jumps and at different temperatures (Supplementary Figures 13 and
 157 14b-d). The fittings for all three studied MOFs show that with increasing temperature, τ
 158 decreases (top panel of Fig. 4b), which is reasonable and has been experimentally demonstrated
 159 for porous electrodes owing to the increase of ion mobility with temperatures^{26,27}. The obtained
 160 value of τ can be used to roughly estimate the charging time, $\tau_0 = \frac{\tau}{(l/L)^2}$, for a practical
 161 supercapacitor cell. For instance, for 1.57-nm-pore MOF-electrode of 100 μm thickness, τ_0 will
 162 be 4.3 and 2.2 seconds at 300 and 400 K, respectively.

163 Specially performed MD-simulations of bulk [EMIM][BF₄] give conductivity of 1.26-8.2 S
 164 m^{-1} within 300-400 K, consistent with experimental data (1.6-10.8 S m^{-1}).²⁸ To evaluate the
 165 conductivity of in-pore RTIL, we extracted the values of τ from fitting Eq. (1) to the MD-
 166 obtained charging curves of Fig. 4a, and then get σ , using Eq. (2). For MOFs with pore sizes of
 167 1.57 and 2.39 nm, σ increases from 0.3-0.9 S m^{-1} within 300-400 K (bottom panel of Fig. 4b).
 168 Interestingly, the conductivity of ions in the smallest pore (0.81 nm), varying within 0.9-1.7 S m^{-1}
 169 in such temperature interval, appears higher than in the other two larger MOF pores. This could
 170 be attributed to the stronger screening electrostatic interactions due to the induced image charges

171 on the pore walls.^{29, 30} Nevertheless, the conductivities of ions under nanoconfinements are
172 obviously smaller than in the bulk.

173 These results suggest considerable limitations for ion transport inside the quasi-1D MOF-
174 pores. Hence, the electrolyte resistance in MOFs would be the dominant contribution to the
175 equivalent series resistance (ESR) of a practical MOF-based EDLC. This is similar to what has
176 been concluded from the experiment with 1.57-nm-pore MOF in an organic solution.¹⁰ It is
177 simply because that the electrical conductivity of this MOF is much higher than the ionic
178 conductivity of RTIL. Interestingly, the larger working voltage results in a decrease of τ and an
179 increase of σ (Supplementary Figure 14e-g), thus promoting faster ion transport inside MOFs.

180 All the above simulations are conducted with RTIL in coarse-grained model³¹ and MOF-
181 electrode in AA interlayer stacking.³² To verify the independence of the model on results, we
182 employed an all-atom model for [EMIM][BF₄] (Supplementary Figure 15).³³ All-atom model
183 gave results very similar to the coarse-grained one, including in-pore ion distributions, charge
184 storage and charging dynamics (Supplementary Figures 16-18). To reveal the effect of interlayer
185 stacking, we performed MD simulations on a slipped-parallel AB stacking model³² of MOF
186 Ni₃(HITP)₂ (Supplementary Figure 19a). The tiny parallel slip (0.137 nm) introduces a negligible
187 difference in both capacitance and charging dynamics (Supplementary Figure 19b).

188 **Capacitive performance at macroscale**

189 To validate MD-obtained capacitance, we, taking MOF Ni₃(HITP)₂ as an example, carried out
190 electrochemical measurements of supercapacitors with [EMIM][BF₄] electrolyte. We have set
191 three synthesis procedures (see Methods), based on previously reported strategies,^{10, 34} and
192 obtained Ni₃(HITP)₂ samples with SSAs of 556, 641 and 732 m² g⁻¹ (Supplementary Figure 20).
193 Scanning electron micrographs demonstrate that the sample with higher SSA has larger rob-like
194 crystallite in the MOF powder (Supplementary Figure 21), indicating enhanced crystallinity,^{8, 35,}
195 ³⁶ as verified by the powder X-ray diffraction patterns of the samples with different SSA
196 (Supplementary Figure 22).

197 Two-electrode cells were fabricated, with these Ni₃(HITP)₂ samples of different crystallinity,
198 to measure the capacitance of this MOF in RTIL [EMIM][BF₄] (for details see Methods). With
199 cyclic voltammogram (CV) measurements at a scan rate of 10 mV s⁻¹ (Fig. 5a, for results at 5

200 mV s⁻¹ see Supplementary Figure 23), we obtained that the gravimetric capacitances for
201 Ni₃(HITP)₂, with SSAs of 556, 641 and 732 m² g⁻¹, are, respectively, 58, 70 and 76 F g⁻¹, which
202 are all smaller than the MD-obtained capacitance of ~101 F g⁻¹ with SSA of 1153 m² g⁻¹. This
203 difference could be ascribed to the different SSAs resulting from the imperfect crystallinity
204 (Supplementary Figures 21-22). The areal capacitance, however, depends little on the SSA (~11
205 μF cm⁻², Supplementary Table 5), and is close to the modeling value of ~9 μF cm⁻². This weak
206 crystallinity-dependent areal capacitance of MOF-electrode suggests that pores accessible to ions
207 contribute equally to charge storage, which is essentially different from typical porous carbons
208 with pores of different size and shape. Accordingly, by improving the MOF crystallinity, one
209 could achieve both larger SSA and higher gravimetric capacitance, closer to the modeling value.

210 The up-to-date conductive MOFs, however, have smaller electrochemical voltage windows
211 (limited by the onset of electrochemical reactions under positive and negative polarizations) than
212 those achieved for metallic electrodes with RTILs.^{5, 6, 7, 8, 10, 13, 14} Our CV measurements of
213 Ni₃(HITP)₂ in a three-electrode cell indicate that enhancing MOF crystallinity, accompanied with
214 SSA increase from 556 to 732 m² g⁻¹, would also enlarge its voltage window from about 2.1 to
215 2.8 V (Supplementary Figure 24). Our cycle-life tests further confirm the increased working
216 voltage with improving crystallinity, although the voltage window shrinks a little
217 (Supplementary Figure 25).

218 We then measured the ESR of MOF-based EDLCs. The galvanostatic charge-discharge
219 (GCD) curve in Fig. 5b was experimentally obtained at room temperature for two-electrode
220 cells composed of 25 μm separator and MOF Ni₃(HITP)₂ pellets with 180 μm thickness and 6.4
221 mm diameter. Then, the ESR was found to be 8.6 Ω cm², similar to our electrochemical
222 impedance spectroscopy (EIS) data (8.9 Ω cm², Supplementary Figure 27). Previous experiments
223 have reported a smaller ESR of this MOF than of porous carbons in organic electrolyte.¹⁰ To
224 identify this advantage of Ni₃(HITP)₂ in RTIL electrolyte, a commercial activated carbon (YP-
225 50F) was chosen for comparison, with nearly the same size and mass loading and without any
226 binders and additives. The ESR for the assembled cells with [EMIM][BF₄] was determined from
227 GCD curves as about 7.2 and 15.9 Ω cm², respectively, for electrodes made of Ni₃(HITP)₂ and
228 activated carbon with Ni foam collectors (Supplementary Figure 26). It was earlier
229 experimentally demonstrated that the electrodes based on aligned single-walled carbon

230 nanotubes show greatly enhanced ion transport parallel to the alignment direction.³⁷ Similarly,
231 the MOFs studied herein, possessing crystal structure and retaining crystallinity when made into
232 electrodes,^{10, 32} could offer straight quasi-cylindrical pores, providing faster charging dynamics
233 than the carbon with tortuous pores and amorphous topology.

234 The MD-obtained capacitance and conductivity of electrolyte in a MOF pore, together with
235 intrinsic properties of MOFs (Supplementary Table 2), could be used to assess the capacitive
236 performance of a ‘practical’ MOF-based supercapacitor, via macroscale equivalent circuit
237 simulations (for details see Methods and Supplementary Part 7). Based on the values of σ and
238 capacitance, for three studied MOFs, Nyquist plots were computed for supercapacitors with the
239 same sized MOF-electrode (180 μm thickness and 6.4 mm diameter) and separator (25 μm
240 thickness). They differ, to some extent, from EIS measurement (Fig. 6a vs. Supplementary
241 Figure 27), as modeling adopts ideal monocrystalline MOF electrodes and neglects the electrode
242 and electrode-collector contact resistances. From simulation-obtained Nyquist plots, ESRs of
243 such cells at 400 K were obtained as 3.1, 2.9 and 2.3 $\Omega \text{ cm}^2$ for MOFs with the pore size of 0.81,
244 1.57 and 2.39 nm, respectively. At 300 K, ESR increases to approximately 6.4 $\Omega \text{ cm}^2$ for three
245 MOF electrodes (Fig. 6b), which is compatible with our experimental values from both GCD and
246 EIS measurements. These results indicate that the ESR of MOF-electrode EDLCs is dominated
247 by the resistances of the in-pore electrolytes. Therefore, molecular modeling is a quite
248 appropriate approach to assessing both charge storage and charging dynamics of MOF
249 supercapacitor at macroscale.

250 Ragone plots for temperature-dependent power-energy relationships are shown in Fig. 6b-c.
251 The temperature has minor influence on maximal energy density but has a large effect on the
252 power density. For applications demanding the best gravimetric performance, MOFs with the
253 largest pore size (2.39 nm) seem to be a better choice, delivering both higher energy and power
254 density, in comparison with the other two MOFs (Fig. 6b). As the temperature increases from
255 300 to 400 K, under a cell voltage of 2.8 V, the MOF with the largest pore size could reach
256 power density of 20-46 kW kg^{-1} and an energy density about 30 Wh kg^{-1} . For optimized
257 volumetric performance, all three MOFs exhibit similar promising performance, with a power
258 density range of 13-30 kW L^{-1} and energy density of $\sim 20 \text{Wh L}^{-1}$. These compare favorably with
259 performance of most reported carbon-based EDLCs (Supplementary Table 6).^{22, 23, 24, 38, 39} As

260 expected, under higher voltages, the energy and power densities would both increase
261 (Supplementary Figure 29).

262 **Conclusion**

263 We have investigated the charge storage and charging dynamics of supercapacitors consisting of
264 conductive MOF electrodes and RTIL electrolyte. The microstructures of RTIL inside MOF
265 pores were analyzed in terms of in-plane (2D) and axial (1D) ion distributions, as well as ion
266 orientations, which help interpret the obtained camel- and bell-shapes of the capacitance-
267 potential dependence. With TML rationalizing the charging dynamics, we evaluated the
268 capacitive performance of macroscale EDLC devices. Modeling results revealed that these
269 MOF/RTIL-based cells could exhibit performance superior to most carbon-based devices,^{22, 23, 24,}
270 ^{38, 39} which suggest promising avenues for designing supercapacitors with both high energy and
271 power densities.

272 The improvement of MOF crystallinity obtained through different synthesis procedures was
273 shown to enlarge not only their SSA and particle size^{8, 35, 36} but also their working voltage. The
274 electrochemical measurements on supercapacitors made of MOF materials solely as electrodes
275 and RTILs as electrolytes have shown that the gravimetric capacitance increases with SSA. The
276 ESR of MOF is quite smaller than similarly structured cell with a typical commercial porous
277 carbon, showing the benefit of the well-controlled monodisperse pore structures in MOFs. Both
278 areal capacitance and resistance obtained in experiment agree with modeling, signifying that our
279 molecular simulation could well represent the real system of MOF-based supercapacitor.

280 Although many conductive MOFs have been synthesized,^{5, 6, 7, 8, 40} they are still a new family
281 in MOF community and more of them require to be developed, which would take the modeling-
282 guided design as key input. Moreover, to be developed 3D conductive MOFs scaffolds might be
283 expected to have advantages over the dense stacks of 2D-MOF-sheets with quasi-1D pores.
284 Indeed, 3D scaffolds could provide ion transport paths in all directions and consequently
285 promote cation-anion swapping, pivotal in charging-discharging processes. Such scaffold-
286 electrodes with the all-dimension openness and high porosity may help enhance the charging
287 dynamics, and together with the enhanced surface area, potentially enlarge energy and power
288 densities simultaneously.

289 **Methods**

290 **Molecular dynamics simulation**

291 As shown in Fig. 1, the MD simulation system consists of two identical and symmetric
292 conductive MOFs immersed in a RTIL [EMIM][BF₄]. Real supercapacitors certainly contain an
293 electronically isolating ion transport membrane that warrants the absence of a short-cut between
294 the electrodes, however, ideal membranes must not impede ion exchange between the electrodes.
295 For this proof-of-the principle study, considering therefore the best performance possible, we
296 will not incorporate the membrane into our simulation cell. This strategy is generally adopted for
297 MD modeling of supercapacitors.^{15, 17, 25, 31, 41} The atomistic structures of MOF Ni₃(HITP)₂ were
298 obtained from experimental measurements,³² and MOFs Ni₃(hexahydroxybenzene)₂ (Ni₃(HHB)₂)
299 and Ni₃(2,3,8,9,14,15-hexaiminotrinaphthalene)₂ (Ni₃(HITN)₂) were constructed, respectively,
300 with reference to Cu₃(HHB)₂ (Ref. ⁴²) and Ni₃(HITP)₂. The geometry optimization of each MOF
301 in Fig. 1c and the partial charge distribution for each MOF in unpolarized state (Supplementary
302 Figure 1) were derived from DFT calculations, using in Vienna ab initio simulation package
303 (VASP)⁴³. Furthermore, the corresponding density of states was computed to demonstrate that all
304 the MOFs studied are conductive (Supplementary Figure 2), though Ni₃(HHB)₂ and Ni₃(HITN)₂
305 have yet been successfully synthesized. Details of MOF structure optimization of MOFs and
306 pore size calculation can be seen in Supplementary Part 1 and Supplementary Tables 1-2. The
307 Lennard-Jones parameters for the MOF atoms were taken from the generic universal force field
308 (UFF)⁴⁴; the coarse-grained model was adopted for [EMIM][BF₄], which could provide the
309 proper thermodynamic and dynamic properties³¹. The simulation cells were chosen as large
310 enough to reproduce the bulk state in the central region of RTIL reservoir connected with two
311 electrodes, and periodic boundary conditions were applied in all directions. Specific system
312 parameters are given in Supplementary Table 3.

313 Simulations were performed in the NVT ensemble using a customized MD software
314 GROMACS.⁴⁵ The applied electrical potential between the two electrodes in Fig. 1 was
315 maintained by the constant potential method (CPM), as it allows the fluctuations of charges on
316 electrode atoms during the simulation.^{15, 31, 41} Details of CPM could be found in Supplementary
317 Part 2. To guarantee the accuracy, the electrode charges are updated on the fly of simulation
318 running at every simulation step (2 fs). The electrolyte temperature was maintained at 400 K

319 using the V-rescale thermostat⁴⁶. The electrostatic interactions were computed using the particle
320 mesh Ewald method⁴⁷. An FFT grid spacing of 0.1 nm and cubic interpolation for charge
321 distribution were used to compute the electrostatic interactions in the reciprocal space. A cutoff
322 length of 1.2 nm was used in the direct summation of the non-electrostatic interactions and
323 electrostatic interactions in the real space. For each conductive MOF, the MD system was
324 annealed from 500 to 400 K over a period of 10 ns, following by running another 40 ns to reach
325 equilibrium under null electrode potential. To explore the charging dynamics, five independent
326 runs were performed for smoothing the charging process data. To obtain microstructure and
327 capacitance, a simulation was performed for 60 ns to surely reach equilibrium under the applied
328 potential ranging from 0 to 6 V, and then another 60 ns production in equilibrium state was run
329 for analysis.

330 In metallic electrodes, before the onset of electrochemical reactions, there are no limitations
331 on accommodating or depleting electrons. Their capacitance is determined by their ability to
332 accumulate the ionic charge from electrolyte. In electrodes built from low dimensional materials,
333 such as graphene and its derivatives, accommodation of electrons has its own laws that give rise
334 to the quantum capacitance (QC) contribution,^{48, 49, 50} when the electrode's QC is much larger
335 than the electrolytic capacitance, the total capacitance will be predominated by the ionic
336 contribution.^{16, 50} Thick dense stacks of 2D MOF sheets, even those that deliver large pores are
337 not electronically low-dimensional. Unless concentration of charge carriers in them is as low as
338 in wide-band-gap semiconductors, they are expected to perform like bulk porous metallic
339 electrodes; our density function theory (DFT) calculations demonstrate that all MOFs studied
340 here are well conductive (Supplementary Figure 2); thus we focus on the ionic contribution.

341 Therefore, the electrode potential was obtained as the potential difference between the
342 electrode and the electrolyte reservoir and calibrated relative to PZC of the electrode, and then
343 the differential capacitance was calculated by taking derivatives of the MD-obtained surface
344 charge density as a function of electrode potential (details can be seen in Supplementary Part 2
345 and Supplementary Figure 4). The electrical conductivity of the bulk [EMIM][BF₄] was
346 evaluated via the time integral of ECACFs, $\sigma_{RTIL} = \frac{1}{3Vk_B T} \int_0^\infty \langle \vec{J}(0) \cdot \vec{J}(t) \rangle dt$, in which V is
347 the system volume and $\vec{J}(t)$ denotes the electrical current. $\vec{J}(t)$ is defined by $\vec{J} = \sum_{i=1}^N q_i \vec{v}_i$,
348 where N is the total number of ions, and q_i and $\vec{v}_i(t)$ are the charge and velocity of the i -th ion,

349 respectively.

350 It is worth noting that static prosperities of EDLCs were studied at a temperature of 400 K
351 that is generally used for MD simulations to get the ion structure and capacitance^{25, 31}, while the
352 charging dynamics was ascertained within a temperature range of 300-400 K due to the big
353 impact of temperature on dynamic properties^{26, 27}.

354 **Equivalent electrical circuit simulation**

355 We conceived a practical size two-electrode symmetric cell (see Supplementary Figure 28a),
356 based on our EDLC cell with Ni₃(HITP)₂ pellet electrodes in experiment. Specifically, the
357 diameter of the MOF electrode was set as 6.4 mm, and the electrode thickness was taken as 180
358 μm for three studied MOFs in Fig. 1. The equivalent circuit model of the conceived two-
359 electrode symmetric cell was based on RC transmission line circuit in which the resistors and the
360 capacitors were calculated based on the size of the cell and the MD-obtained specific capacitance
361 and conductivity of ions in MOF. The circuit simulations were performed via *Simulink*, in which
362 impedance measurement and constant power load (via boosting DC-DC converter block) tests
363 were carried out respectively to obtain the Nyquist plots and Ragone plots for three MOF-based
364 EDLCs in practical cell size. Detail can be seen in Supplementary Part 8 with Supplementary
365 Figure 28.

366 **Materials for experiments**

367 All the starting materials were purchased from commercial suppliers. Specifically, 2,3,6,7,10,11-
368 hexaaminotriphenylene hexahydrochloride (HATP·6HCl) was purchased from Alfa; NiCl₂·6H₂O
369 was purchased from Sigma-Aldrich; Concentrated aqueous ammonia was purchased from TCI;
370 Ethanol and acetone were purchased from Sinopharm. RTIL [EMIM][BF₄] was purchased from
371 Aladdin. Starting materials were used without further purification unless otherwise noted.
372 Activated carbon was purchased from Kurary Chemical, taken to compare with MOF electrode
373 material.

374 **Synthesis of MOFs**

375 Based on synthesis strategies reported in the previous work,^{10, 34} we obtained electrode materials
376 of Ni₃(HITP)₂ with different surface areas of 556, 641, and 732 m² g⁻¹, through three different

377 procedures which are given below.

378 Procedure I: A solution of 323 mg (1.36 mmol) of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in 20 ml of water was added
379 to a solution of 487 mg (0.91 mmol) of HATP·6HCl in 140 ml of water. Through this work, all
380 the water used was deionized. Then 4.5 ml of concentrated aqueous ammonia (NH_4OH , 14.79
381 mol l^{-1}) was added to the mixture. The mixture was stirred in a flask under air bubbling for 1 h at
382 60 °C, then air bubbling was turned off and the mixture was stirred for an additional 2 h at 60 °C.
383 The resulting black powder was isolated by centrifugation immediately and washed with water
384 (2 times, 180 ml) and ethanol (2 times, 180 ml). The solid was then dried under vacuum for 12 h
385 at 150 °C. The product was kept in refrigerator.

386 Procedure II: A solution of 162.1 mg (0.675 mmol) of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in 10 ml of water was
387 added to a solution of 243.7 mg (0.453 mmol) of HATP·6HCl in 70 ml of water. Then 2.25 ml of
388 NH_4OH (14 mol l^{-1}) was added to the mixture. The mixture was stirred in a flask under air
389 bubbling for 1 h at 60 °C, then air bubbling was turned off and the mixture was stirred for an
390 additional 2 h at 60 °C. The resulting suspension was cooled in air for 1.5 h. The resulting black
391 powder was isolated by centrifugation and washed with water (2 times, 90 ml) and ethanol (2
392 times, 90 ml). The solid was then dried under vacuum for 8 h at 100 °C. After cooling, it was
393 dried under vacuum for an additional 12 h at 100 °C. The product was kept in an argon-filled
394 glovebox.

395 Procedure III: A solution of 96.5 mg (0.406 mmol) of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in 10 ml of water was
396 added to a solution of 142.0 mg (0.264 mmol) of HATP·6HCl in 50 ml of water in a 250-ml
397 Schlenk bottle. The resulting yellow solution was stirred manually, heated to 65 °C in an oil bath
398 and treated with 1.5 ml of NH_4OH (14.79 mol l^{-1}). The reaction mixture was kept at 65 °C for 45
399 min under continuous air bubbling upon which the reaction was switched to an N_2 atmosphere
400 and kept at 65 °C for an additional 2 h. The resulting suspension was cooled in an N_2 atmosphere
401 for 2 h. The resulting black powder was separated from the reaction mixture by centrifugation,
402 soaked in water at room temperature for 18 h, and washed with water (2 times, 180 ml), ethanol
403 (2 times, 180 ml) and acetone (2 times, 180 ml). Finally the solid product was dried under a
404 stream of nitrogen gas for 12 h. The product was kept in an argon-filled glovebox.

405 **Characterization of MOF powder**

406 Nitrogen adsorption/desorption isotherms were measured with a Quantachrome Autosorb IQ
407 system at 77 K. Before the gas adsorption/desorption measurement, as-synthesized MOFs (~100
408 mg) samples were activated by drying under vacuum for 12 h at 100 °C. Afterwards, liquid
409 nitrogen baths (77 K) were used to measure nitrogen adsorption/desorption isotherms. The free
410 space correction and measurement were conducted using ultrahigh-purity grade (99.999% purity)
411 nitrogen and helium, oil-free valves, and gas regulators. Powder X-ray direction (PXRD)
412 patterns were carried out with a PANalytical Empyrean X-ray Powder diffractometer equipped
413 with a Cu-sealed tube ($\lambda = 1.544426 \text{ \AA}$) at 40 kV and 40 mA, and samples were prepared on a
414 zero-background silicon crystal plate. Scanning electron microscopy (SEM) observation was
415 performed with a Zeiss Gemini 300 SEM with an operating voltage of 3 kV. Transmission
416 electron microscopy (TEM) was performed on a FEI Tecnai G2 F20 microscope and operated at
417 300 kV (point resolution 80 pm). Samples for TEM were dispersed in acetone, and a droplet of
418 the suspension was transferred onto a carbon coated copper grid.

419 **Electrochemical measurement and analysis of MOF electrodes**

420 A two-electrode cell was fabricated to measure the capacitive performance of MOF electrodes in
421 an Argonne-filled glovebox. Prior to electrochemical measurement, electrolyte [EMIM][BF₄]
422 was vacuum-dried for 12 hours at 100 °C and then was treated with ultrapure argon (99.999%) to
423 remove absorbed water and dissolved gas as much as possible. The cell is assumed to be
424 symmetric, since the difference of MOF materials in two electrodes was controlled within 5%.
425 All electrochemical measurements were performed on a Zahner Zennium electrochemical
426 workstation.

427 Through this work, all the MOF electrodes were fabricated without any binders or
428 conductive additives. To measure the capacitance, MOF powders were compressed into a Ni
429 foam working electrode with a mass loading of $\sim 4 \text{ mg cm}^{-2}$. We calculated the gravimetric
430 capacitance (C_g) of one single electrode from the cyclic voltammetry curves, according to the
431 following equation:

$$432 \quad C_g = 4 \frac{\int_0^{V_0/v} I dt}{V_0 m} \quad (3)$$

433 where I and v are the discharge current and the scan rate, respectively, V_0 is the operating
434 voltage, and m is the total active material mass of both electrodes in the symmetric cell.

435 The experimental gravimetric capacitance (C_g) can be compared with MD-obtained integral
436 capacitance (C_g^{MD}). C_g^{MD} can be obtained directly from the CPM simulation that is performed
437 under V_0 potential drop between the two electrodes, as $C_g^{MD} = 4 \frac{Q}{V_0 m}$, in which Q is the total
438 charge on one electrode. To obtain the ESR, the electrode made of MOF pellets in 6.4 mm
439 diameter and 180 μm thickness (mass loading $\sim 5.9 \text{ mg cm}^{-2}$) on a 25- μm -thick Au foil. Through
440 galvanostatic charge-discharge measurements, we computed the ESR from the voltage drop
441 (V_{drop}) at the beginning of the discharge curve by $\text{ESR}(\Omega) = (V_{drop}/2I)$, where I is the constant
442 discharge current.

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568

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578 **Author contributions**

579 G.F. and A.A.K. set the strategy of this project in consultation with M.D.; G.F. devised simulation
580 approaches; G.F. and M.D. designed the experiment. S.B. performed major part of molecular dynamics
581 simulations with participation of M.C., R.X.W. and J.M.F.; M.C. did all DFT calculations; H.B., L.N.,
582 M.Y.C., T.Z.W., J.S.W., and T.Y.C. carried out the experiment in which L.N. developed MOF synthesis
583 procedures; G.F., S.B., M.C., L.N., M.Y.C. and A.A.K. analyzed the data and wrote the manuscript; G.F.,
584 S.B., A.A.K., M.C., H.B., and M.D. contributed to the discussion of results, editing and revising the paper.

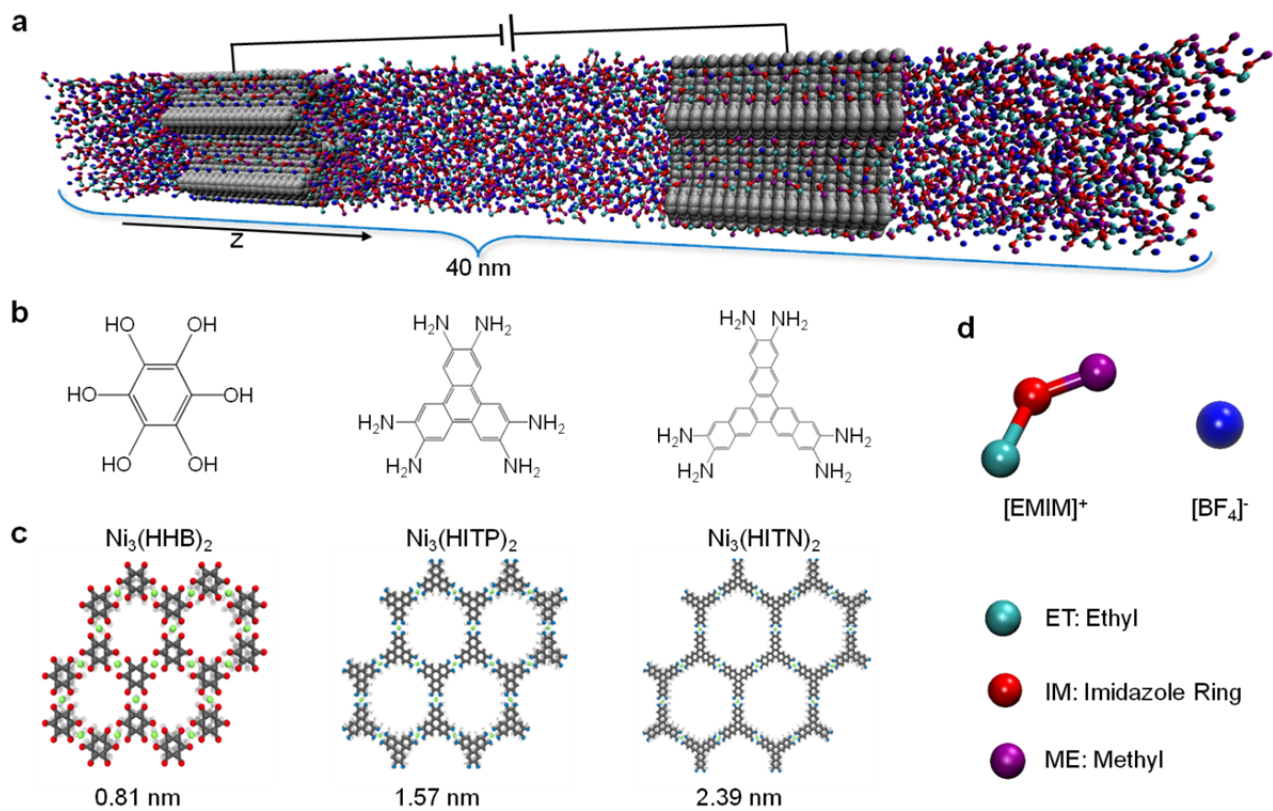
585 **Additional information**

586 Supplementary information is available for this paper at ...

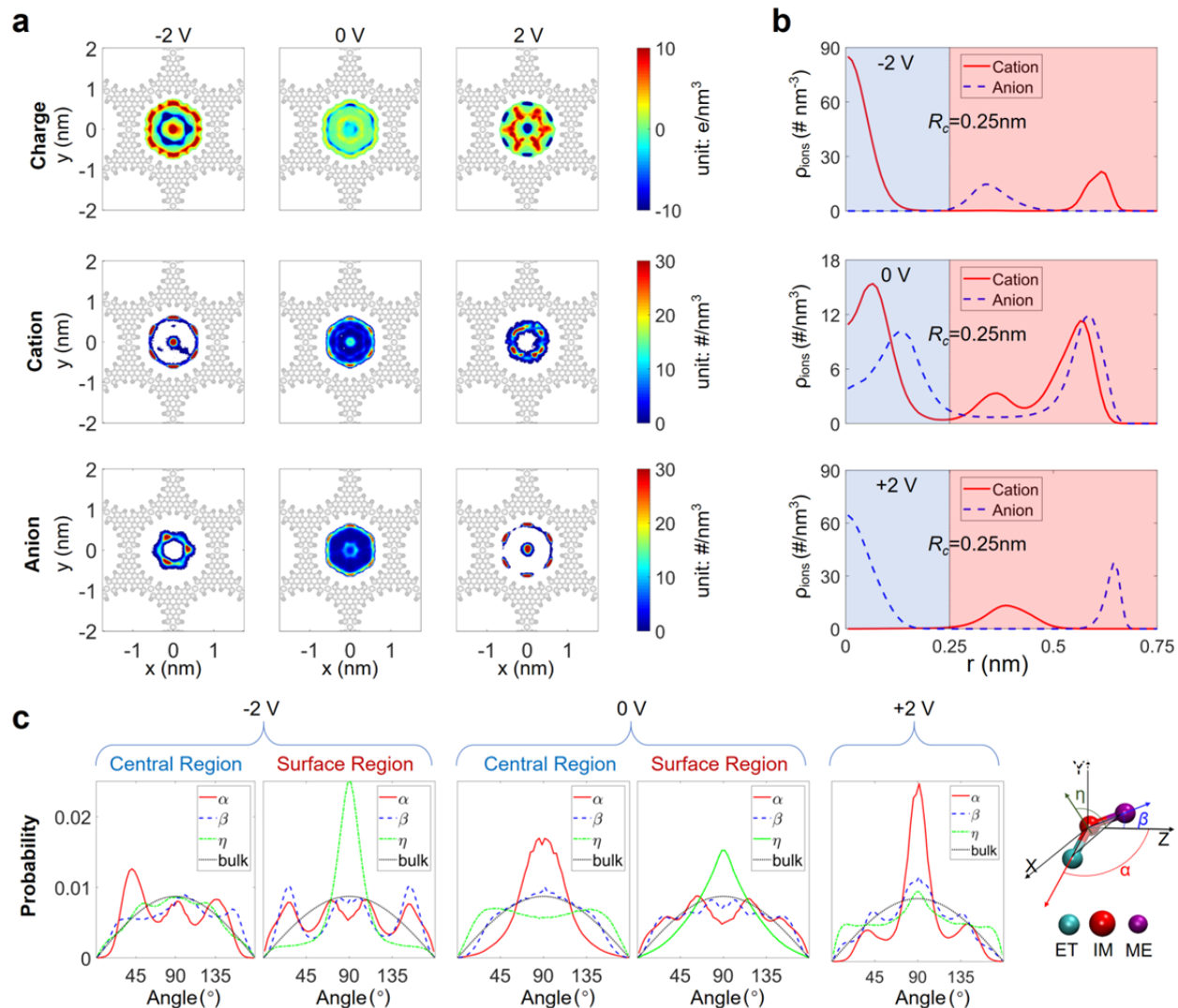
587 **Competing interests**

588 The authors declare no competing interests.

589 **Figure 1**

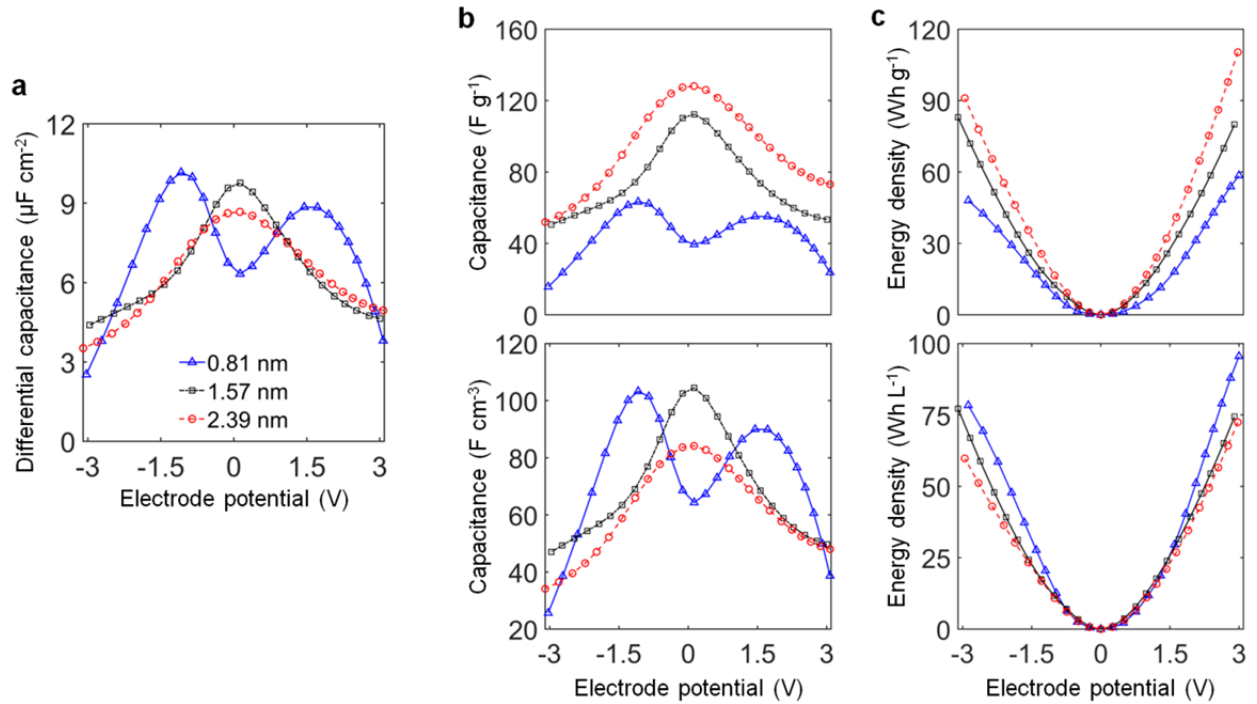


590
 591 **Fig. 1 | Schematics of MD simulation of MOF-based supercapacitors.** **a**, A snapshot of the simulation
 592 system containing two identical MOF electrodes connected with RTIL reservoirs (periodically repeated in
 593 all three dimensions). Each electrode has stacks of eighteen 2D MOF sheets. **b**, Molecular structures of
 594 the linkers used for three studied MOFs. **c**, 2D honeycomb structures of MOF sheets studied. The
 595 numbers at the bottom indicate characteristic in-plane sizes of quasi-1D pores formed by the stacked
 596 MOF sheets (i.e., effective pore diameters). **d**, Coarse-grained model of RTIL [EMIM][BF₄]. Details for
 597 all three studied MOFs and simulation setup can be found in Supplementary Part 1 and Supplementary
 598 Tables 1-3.



600
 601 **Fig. 2 | In-pore charge/ion density and orientation distributions.** **a**, In-plane, 2D maps of charge and
 602 ion distributions of [EMIM][BF₄] inside a pore of a studied MOF. Each map is based on simulation data
 603 averaged along the pore axis (pore diameter is 1.57 nm). Columns correspond to three (indicated)
 604 electrode potentials (0 V means PZC, see the main text) and rows indicate 2D charge distributions (up
 605 row) and 2D number density distributions of cations (middle row) and anions (bottom row). For better
 606 visibility, results for neighboring pores are not displayed, and in the central pore the areas where no ions
 607 could access are shown in white. **b**, Radial ion distributions of ion inside pore. $r = 0$ stands for the pore
 608 centre. The light blue and red shaded areas, separated by a critical value of radial distance ($R_c = 0.25 \text{ nm}$),
 609 represent the central and surface regions of the pore space. **c**, Angular distribution of cations located in
 610 central and surface regions of the MOF pore.

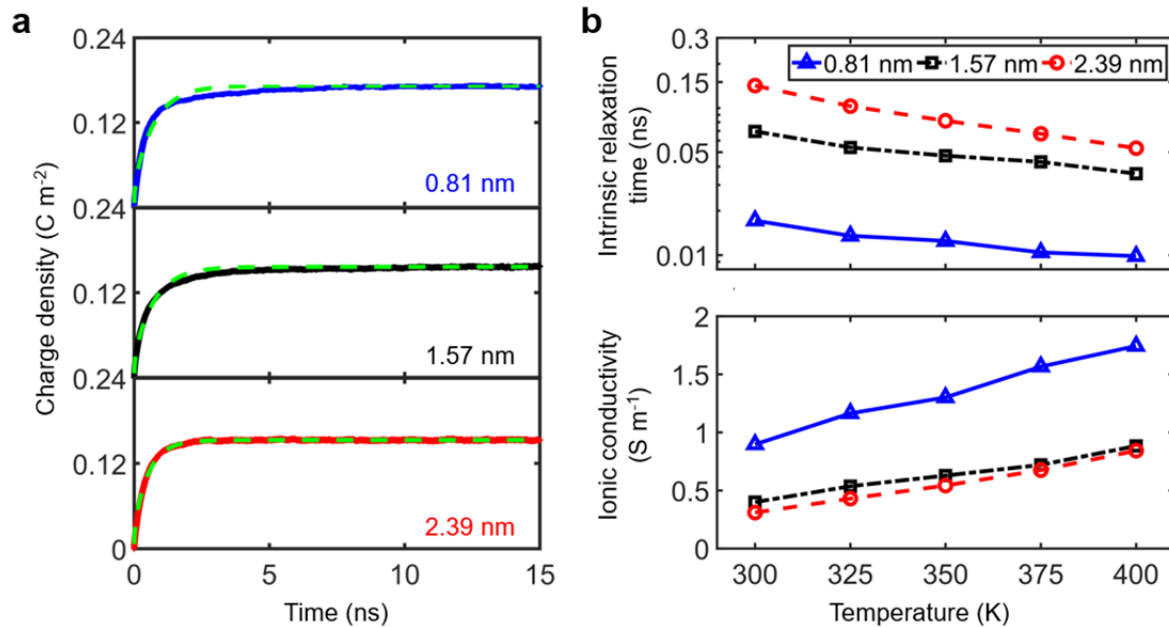
611 **Figure 3**



612

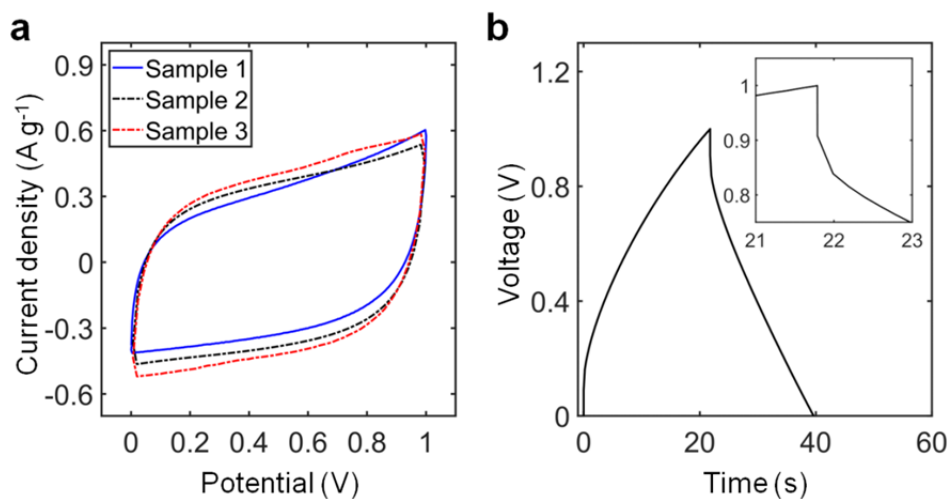
613 **Fig. 3 | Capacitance and energy density.** Voltage dependence of the capacitance of ionic-liquid-filled
 614 MOF electrode and the stored energy density. **a**, Differential capacitance per unit pore surface area. **b-c**,
 615 Gravimetric (**b**) and volumetric (**c**) capacitance and energy density of three studied MOFs. The energy
 616 density is calculated by $E_{g/v}(\varphi) = \int \varphi C_{g/v}(\varphi) d\varphi$, where $C_{g/v}$ is the gravimetric/volumetric capacitance.

617 **Figure 4**



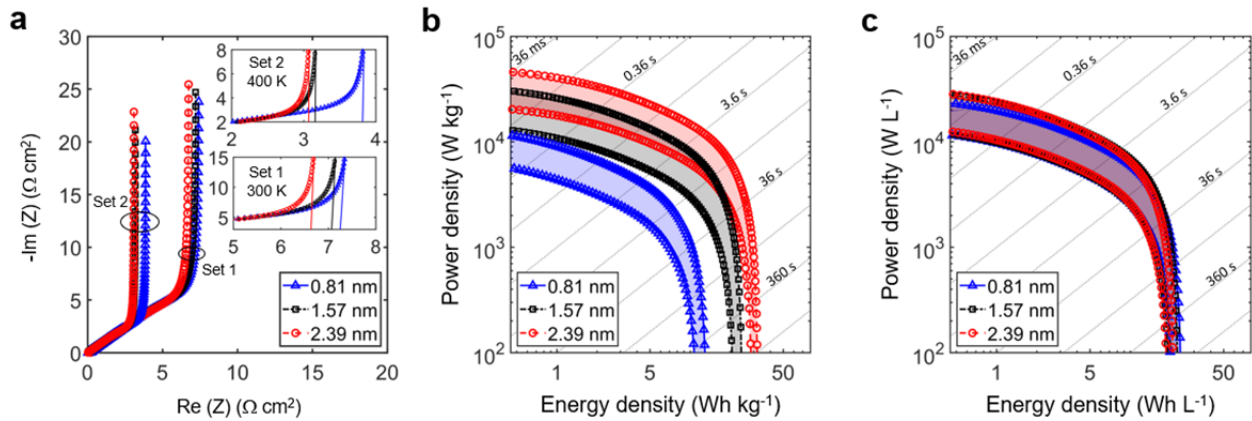
618
 619 **Fig. 4 | Charging process at nanoscale.** **a**, Time evolution of charge density per unit surface area of the
 620 pore, after a cell voltage of 4 V was applied between two electrodes, shown for the positive electrode, for
 621 three MOFs of indicated pore sizes at 400 K. MD-obtained results are shown against the curves (green
 622 dashed lines) fitted by the transmission line model sketched in Supplementary Figure 12a. **b**, Intrinsic
 623 relaxation time (top panel, shown in logarithmic scale for better visibility) and the ionic conductivity
 624 (bottom panel) of RTILs in the MOF pores at different temperature.

625 **Figure 5**



626
627 **Fig. 5 | Capacitive measurement of Ni₃(HITP)₂ electrodes in a symmetrical supercapacitor**
628 **cell. a,** Cyclic voltammograms at a scan rate of 10 mV s⁻¹. Sample 1, 2, and 3 have specific
629 surface areas of 556, 641, and 732 m² g⁻¹, respectively. **b,** Galvanostatic charge and discharge
630 curve of two-electrode cells with pellet MOF Ni₃(HITP)₂ at a current density of 0.5 A g⁻¹. Inset
631 enucleates how to determine the ESR from the potential drop at the beginning of a constant
632 current discharge.

633 **Figure 6**



634
 635 **Fig. 6 | Capacitive performance predicted for practical cell-size supercapacitors. a,** Nyquist plots for
 636 MOF-based supercapacitors at temperatures of 300 K (Set 1) and 400 K (Set 2). **b-c,** Gravimetric (**b**) and
 637 volumetric (**c**) Ragone plots for MOF-based supercapacitors from 300 to 400 K. Blue triangles, black
 638 squares, and red dots represent results for MOFs with the pore sizes of 0.81, 1.57, and 2.39 nm,
 639 respectively. Grey dotted lines in **b-c** indicate the lasting time that quantifies how long a supercapacitor
 640 can supply the power at an appointed power-energy point. The voltage between cathode and anode is 2.8
 641 V.