Electronic Supplementary Information

Sequential Structural Transformation of Heptanuclear Zinc Cluster towards Hierarchically Porous Carbon for Supercapacitor Applications

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1. Materials and Methods

Synthesis of Zn\(_7\), Zn\(_7\)(C\(_9\)H\(_{10}\)NO\(_2\))\(_6\)(OCH\(_3\))\(_6\)(NO\(_3\))\(_2\)

A mixture of HL (L=2-Methoxy-6-Methylmethyleneaminophenol, 496.0 mg, 3 mmol) and Zn(NO\(_3\))\(_2\)·6H\(_2\)O (1.2 g, 4 mmol) was dissolved in 30.0 mL methanol at room temperature and stirred for about 10 min. Then the mixture was transferred to a Teflon-lined steel bomb and heated by microwave at 100 °C for 30 min. The autoclave was then cooled at a rate of 10 °C·h\(^{-1}\). Light yellow crystals were collected by filtration, washed with methanol, and dried in air. Yield: 40 mg, 30 % (based on Zn). Elemental analyses (%) calculated for Zn\(_7\): C 41.10, H 4.48, N 6.39. Found: C 40.9, H 4.53, N 6.35. IR data for Zn\(_7\) (KBr, cm\(^{-1}\)): 3425.6(s), 2920.5(m), 1629.8(s), 1472.4(s), 1320.7(m), 1226.3(s), 1071.8(m), 963(m), 742.6(s).

Characterization

Thermogravimetric analyses (TGA) were performed under a flow of nitrogen at a heating rate of 5 °C min\(^{-1}\) using a Netzsch TG 209 F3. Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku D/max-III A diffractometer (Cu K\(\alpha\)) at 293 K. Ex-situ SAXS patterns were recorded at 50 kV, 0.6 mA on Nanostar U SAXS, the wavelength of X-ray is 0.154 nm. X-ray photoelectron spectroscopy (XPS) were conducted on VG Microtech ESCA 2000 using a monochromic Al X-ray source, and the binding energies (BE) were calibrated by setting the measured binding energy of C 1s to 284.8 eV. Raman spectra were collected by a Renishaw System 1000 micro-Raman spectroscope. Inductive Coupled Plasma Emission Spectrometer (ICP) was performed on Agilent 5110 ICP-OES. The N\(_2\) adsorption-desorption isotherms were collected using a Quantachrome Instruments Autosorb-iQ2-MP at 77 K. Prior to the measurement, the samples were degassed at 200 °C. The surface area of the samples was estimated by method of Brunauer-Emmett-Teller (BET) and the estimation of the distribution of mesoporous and microporous was made by application of the Density-Functional-Theory (DFT) method to the adsorption data. Raman spectra were collected on a Renishaw System 1000 micro-Raman spectrometer.

The thermogravimetric-mass analysis was performed on a Rigaku Thermo Mass Photo TG-MS with a Skimmer type mass spectrometer (MS/EI). The measurements
were conducted in the range 30-900 °C at 5 K·min⁻¹. The samples were finally cooled down to room temperature. The weight of initial samples was about 3.0 mg, and the whole experiment was conducted under inert gas atmosphere with a helium gas flow of 100 mL·min⁻¹.

**X-ray Crystallography**

Single-crystal X-ray diffraction data for Zn₇ were collected on a Rigaku R-AXIS SPIDER IP diffractometer employing graphite-monochromated (Cu, $\lambda = 1.54184 \, \text{Å}$) using the $\theta$-$\omega$ scan technique at 100 K. The structure was solved by direct methods using ShelXS and refined using full-matrix least-squares technique within the SHELXL2015 and OLEX2 program packages. All non-hydrogen atoms were refined with anisotropic thermal factors. Crystallographic data for the structural analyses have been deposited at the Cambridge Crystallographic Data Center and given CCDC reference number 2020712. The supplementary crystallographic data for this compound can be found in the Table S1a, and selected bond lengths and angles are given in Table S1b.

**X-ray total scattering and pair distribution function (PDF) analysis**

X-ray total scattering data were collected at room temperature using Rigaku SmartLab X-ray diffractometer with Ag-source ($\lambda=0.56 \, \text{Å}$). Data collection was carried out using loaded 0.7 mm diameter quartz capillaries and collections conditions were: 3-157 ° in 2θ, 0.05 ° step size, 0.5 °·min⁻¹. Corrections for background, multiple scattering, container scattering, and absorption were applied using the SmartLab studio II.

**Electrochemical Measurements.**

The measurements were performed on a CHI 760E electrochemical workstation using a three-electrode configuration with glassy carbon working, platinum foil counter and Ag/AgCl reference (saturated with KCl solution) electrodes. The as-prepared carbon materials were coated on the surface of the glassy carbon electrode with Nafion solution. The mass loading of active materials for the electrochemical test is 0.71 mg·cm⁻². Cyclic voltammograms at different sweep rates of 5 to 100 mV·s⁻¹ with 0.5 mol·L⁻¹ H₂SO₄ as supporting electrolyte.
Galvanostatic charge/discharge tests at various current densities were performed with voltage ranging from -0.6 to 1.0 V.

\[ C_m = \frac{I \times \Delta t}{\Delta V} \quad (1) \]

Where \( C_m \) is the specific capacitance (F g\(^{-1}\)) and \( I \) is the current density (A g\(^{-1}\)), \( \Delta t \) is the discharge time (s) and \( \Delta V \) is the potential window (V) that we used.

For kinetic analysis, the capacitance from CV curves was calculated according to the following equation:

\[
\begin{align*}
C &= \frac{1}{\Delta V \times v \times m \times 2} \int_{V_i}^{V_f} idv \\
&= \frac{1}{\Delta V} \int_{V_i}^{V_f} i dv 
\end{align*}
\]

where \( i \) is the discharge current, \( V_i \) and \( V_f \) are initial and final potentials of CV tests, \( \Delta V \) is the potential difference, \( v \) is the scan rate and \( m \) is the mass of as-prepared carbon materials.\[S1\]

We used the Dunn’s method to quantify the capacitance contribution from fast-kinetic processes (including electrical double layer capacitive processes and fast redox reactions) and slow-kinetic processes (redox reactions that are diffusion-controlled).

First, the current density at a fixed potential and a scan rate, \( i \), was extracted from the CV curves. According to Wang et al.,\[S2\] the current density, \( i \), is a function of the scan rate, \( v \), and can be expressed as the sum of two terms \( v \):

\[ i(v) = k_1 v + k_2 v^{0.5} \quad (3) \]

where \( k_1 \) and \( k_2 \) are constants. The first term \( k_1 v \) equals the current density contributed from fast-kinetic processes and the second term \( k_2 v^{0.5} \) is the current density associated with slow-kinetic (or diffusion-controlled) processes. By dividing \( v^{0.5} \) on both sides of the equation, it yields:

\[ i \frac{v^{0.5}}{v^{0.5}} = k_1 v^{0.5} + k_2 \]

Therefore, \( i v^{0.5} \) and \( v^{0.5} \) are expected to have a linear relationship. The slope equals \( k_1 \) and the y-intercept equals \( k_2 \). By repeating the above steps for other potentials and scan rates, the capacitance contribution from the fast-kinetic and slow-kinetic processes can be quantified.
processes can be mapped out.

The $b$-value analysis was performed to evaluate the charge-storage kinetics of the electrodes by cyclic voltammetry. According to Augustyn et al.,$^{[53]}$ the current densities at different scan rates and a fixed potential obey the following power-law relationship:

$$i(v) = kv^b \quad (5)$$

where $k$ is a pre-exponential constant and $b$ is a real number between 0.5 and 1.0. When $b$ equals 0.5, the charge-storage processes are sluggish due to the slow ion diffusion within the electrode. For instance, most ion-battery electrodes store charges via slow solid-state ion diffusion and thus their $b$ values typically approximate to 0.5. When $b$ equals 1.0, the charge-storage processes are rapid and are not diffusion limited. For supercapacitor electrodes that store charges via surface reaction/sorption, solid-state diffusion is not involved and thus the $b$ values are expected to be close to 1.0. For pseudocapacitor electrodes that involve ion diffusion across a thick layer of transition metal oxides, the $b$ values deviate from 1.0. Typically, large deviations of the $b$ values from one signify slow electron conduction and/or ion diffusion.

To obtain the $b$ value, one can take logarithm on both sides of Supporting Equation 5 and convert it to the following:

$$\log i = b \log v + C \quad (6)$$

where $C$ is a constant that equals $\log_{10} k$. Based on Supporting Equation 6, a linear relationship shall be observed between $i$ and $v$ in a logarithmic scale. The $b$ value is the slope of the best linear fitting line.

Electrochemical impedance spectroscopy (EIS) data were collected under the open circuit potentials with an AC amplitude of 10 mV oscillating in the frequency range 100 kHz to 100 MHz.
2. Supplementary Figures and Tables

Table S1a. Crystallographic data for Zn$_7$.

| Compound | Zn$_7$ |
|----------|--------|
| Formula | C$_{60}$H$_{78}$N$_8$O$_{24}$Zn$_7$ |
| Formula weight | 1752.89 |
| T (K) | 293 |
| Crystal system | Trigonal |
| Space group | P-3c$_1$ |
| a (Å) | 14.0680(2) |
| b (Å) | 14.0680(2) |
| c (Å) | 23.3614(4) |
| α (°) | 90 |
| β (°) | 90 |
| γ (°) | 120 |
| V (Å$^3$) | 4004.00(13) |
| Z | 2 |
| $D_c$ (g cm$^{-3}$) | 1.454 |
| μ (mm$^{-1}$) | 2.91 |
| Reflns coll. | 13565 |
| Unique reflns. | 2758 |
| $R_{int}$ | 0.038 |
| $R_f[1 ≥ 2σ(I)]$ | 0.055 |
| $wR_f^2$ (all data) | 0.175 |
| GOF | 1.08 |

$^aR_f = \frac{\sum|F_o| - |F_c||\Sigma|F_o|}{\sum|F_o|}$. $^bwR_f^2 = [\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]^{1/2}$. 
Table S1b. Selected bond lengths (Å) and angles (°) for Zn7.

| Bond                  | Length (Å) | Bond                  | Length (Å) |
|-----------------------|------------|-----------------------|------------|
| Zn1—O3                | 2.126(2)   | Zn2—O1                | 2.416(3)   |
| Zn2—O2\(^v\)          | 2.043(2)   | Zn2—O2                | 2.052(2)   |
| Zn2—O3                | 2.037(2)   | Zn2—O3\(^v\)          | 2.131(2)   |
| Zn2—N1\(^v\)          | 2.091(3)   |                       |            |
| O3—Zn1—O3\(^v\)      | 82.24(8)   | O3\(^v\)—Zn2—O1      | 94.69(11)  |
| O3\(^iii\)—Zn1—O3\(^iv\) | 82.24(8) | O3—Zn2—O2\(^v\)      | 113.06(10) |
| O3\(^i\)—Zn1—O3\(^iv\) | 82.24(8)  | O3—Zn2—O2            | 80.54(9)   |
| O3\(^v\)—Zn1—O3\(^iv\) | 97.76(8)  | O3—Zn2—O3\(^v\)      | 84.25(12)  |
| O3\(^ii\)—Zn1—O3\(^iv\) | 97.76(8)  | O3—Zn2—N1\(^v\)      | 103.48(13) |
| O3\(^i\)—Zn1—O3      | 97.76(8)   | N1\(^v\)—Zn2—O1      | 84.68(14)  |
| O3—Zn1—O3\(^ii\)     | 97.76(8)   |                       |            |
| O3\(^ii\)—Zn1—O3\(^ii\) | 82.24(8)  | C1—O1—Zn2            | 126.4(3)   |
| O3\(^ii\)—Zn1—O3     | 82.24(8)   | C2—O1—Zn2            | 111.2(2)   |
| O3\(^i\)—Zn1—O3\(^v\) | 82.24(8)  | Zn2\(^ii\)—O2—Zn2   | 101.14(10) |
| O3\(^ii\)—Zn1—O3\(^v\) | 97.76(8)  | C7—O2—Zn2\(^ii\)    | 129.2(2)   |
| O2—Zn2—O1            | 70.50(10)  | C7—O2—Zn2            | 124.6(2)   |
| O2\(^v\)—Zn2—O1      | 95.07(11)  | Zn1—O3—Zn2\(^ii\)   | 94.68(9)   |
| O2\(^v\)—Zn2—O2      | 163.26(6)  | Zn2—O3—Zn1           | 97.51(10)  |
| O2—Zn2—O3\(^v\)      | 93.81(10)  | Zn2—O3—Zn2\(^ii\)   | 98.69(9)   |
| O2\(^v\)—Zn2—O3\(^v\) | 78.56(9)   | C10—O3—Zn1           | 123.6(3)   |
| O2—Zn2—N1\(^v\)      | 99.94(13)  | C10—O3—Zn2\(^ii\)   | 120.3(3)   |
| O2\(^v\)—Zn2—N1\(^v\) | 86.69(12) | C10—O3—Zn2           | 116.6(3)   |

Symmetry codes: (i) \(-y+2, x-y+1, z\); (ii) \(y, -x+y+1, -z+1\); (iii) \(-x+y+1, -x+2, z\); (iv) \(-x+2, \ldots\)
\( -y+2, -z+1; \) (v) \( x-y+1, x, -z+1; \) (vi) \( -y+1, x-y+1, z; \) (vii) \( -x+y, -x+1, z. \)

**Table S1b.** Selected bond lengths (Å) for Zn$_7$.

| Bond         | Distance (Å) |
|--------------|--------------|
| O1—C1        | 1.428(5)     |
| O2—C7        | 1.310(4)     |
| O3—C10       | 1.465(5)     |
| N1—C8        | 1.278(5)     |
| O1—C2        | 1.392(5)     |
| N1—C9        | 1.462(6)     |
| N1—C8        | 1.278(5)     |
Table S2. Weight loss calculation for TG in the temperature range of 205 to 280 °C.

\[
\text{Theoretical weight loss percentage} = \frac{\text{Molecular weight of lost fragment}}{\text{Molecular weight of Zn}_7} \times 100 \% \quad (6)
\]

We systematically calculate the data from TG-MS of \( \text{Zn}_7 \) and deduce the possible reactions in this pyrolysis process. First, for each formula unit of \( \text{Zn}_7 \) all two \( \text{NO}_3^- \) anions are dissociated (\(2\text{NO}_3^- = 2\text{NO}_2 + \text{O}_2, \text{NO}_2 + \text{C} = 2\text{NO} + \text{CO}_2\)). Second, the twelve \( \text{CH}_3^+ \) groups produced by the cleavage of six ligands and six methoxy groups in the cationic heptanuclear cluster (\( \text{Zn}_7 \)).

| Name of lost fragment | Number of lost fragment | Molecular weight of lost fragment |
|-----------------------|-------------------------|----------------------------------|
| \( \text{CH}_3^+ \)   | 12                      | 15                               |
| \( \text{NO}_3^- \)   | 2                       | 62                               |

Among them, the molecular weight of \( \text{Zn}_7 \) is 1752.89. Therefore, the theoretical weight loss percentage in the temperature range of 225 to 340 °C is:

\[
\frac{12 \times 15 + 2 \times 46 + 32}{1752.89} \times 100 \% = 17.34 \%
\]

By comparison, the percentage of weight loss in the temperature range of 205 to 280 °C obtained from the thermogravimetric curve data is 17.97 %, which is only 0.63 % different from the theoretical value.
Table S3. Weight loss calculation in the temperature range of 480 to 585 °C.

\[
7\text{ZnO} + \frac{7}{2}\text{C} = 7\text{Zn} + \frac{7}{2}\text{CO}_2 \quad (7)
\]

According to reasonable inference, in the process, all zinc ions are converted into ZnO in one \(\text{Zn}_7\) molecule. Therefore, the coefficient of ZnO in the reaction formula (7) is 7.

| Name of lost fragment | Number of lost fragment | Molecular weight of lost fragment |
|-----------------------|-------------------------|----------------------------------|
| \(\text{CO}_2^+\)     | 7/2                     | 44                               |

Among them, the molecular weight of \(\text{Zn}_7\) is 1752.89. From equation (6), the theoretical weight loss percentage in the temperature range of 480 to 585 °C is:

\[
\frac{3.5 \times 44}{1752.89} \times 100 \% = 8.78 \%
\]

By comparison, the percentage of weight loss in the temperature range of 480 to 585 °C obtained from the thermogravimetric curve data is 8.88 %, which is only 0.1 % different from the theoretical value.
**Figure S1.** The IR spectrum of $\text{Zn}_7$. 
Figure S2. (a) Structure of Zn$_7$, (b) intramolecular hydrogen bond; (c) illustrative representation of the link between Zn$_7$ centers.
Figure S3. (a), (b) SEM images of Zn$_7$, (c) Simulated crystal morphology of Zn$_7$, the exposed crystallographic planes are given for all crystal morphologies; (d) (002) crystallographic plane; (e) (100) crystallographic plane; (f) (010) crystallographic plane.
Figure S4. (a) Powder XRD patterns of Zn$\gamma$, Zn$\gamma$-280, Zn$\gamma$-330, Zn$\gamma$-380, Zn$\gamma$-430, Zn$\gamma$-480; (b) Powder XRD patterns of Zn$\gamma$-600, Zn$\gamma$-700, Zn$\gamma$-800 and Zn$\gamma$-900.
Figure S5. Ex-situ SAXS of Zn$_7$-900, Zn$_7$-1000, and Zn$_7$-1100.
Figure S6. HRTEM images of (a) Zn$_7$-900 (b) Zn$_7$-1000, and (c) Zn$_7$-1100.
Figure S7. Raman spectrum of $\text{Zn}_7$-900, $\text{Zn}_7$-1000, and $\text{Zn}_7$-1100.
Table S4. ICP data of Zn residual within the sample.

| Samples     | Mass fraction of Zn (%) |
|-------------|-------------------------|
| Zn_7-900    | 0.3553                  |
| Zn_7-1000   | 0.0918                  |
| Zn_7-1100   | 0.1089                  |
Figure S8. High resolution XPS spectra of Zn\textsubscript{7}-900, Zn\textsubscript{7}-1000 and Zn\textsubscript{7}-1100.
Figure S9. High resolution XPS spectra of C 1s peak of (a) Zn7-900, (b) Zn7-1000 and (c) Zn7-1100.
Figure S10. High resolution XPS spectra of O 1s peak of (a) Zn$_7$-900, (b) Zn$_7$-1000 and (c) Zn$_7$-1100.
**Figure S11.** High resolution XPS spectra of N 1s peak of (a) Zn$_7$-900, (b) Zn$_7$-1000, (c) Zn$_7$-1100, and (d) the proportion of pyridinic-N, pyrrolic-N and graphitic-N in Zn$_7$-900, Zn$_7$-1000 and Zn$_7$-1100, respectively.
Figure S12. Pore structure analysis. N\textsubscript{2} sorption isotherms of (a) Zn\textsubscript{γ-900}, (b) Zn\textsubscript{γ-1000} and (c) Zn\textsubscript{γ-1100}. (d) Comparison of Zn\textsubscript{γ-900}, Zn\textsubscript{γ-1000} and Zn\textsubscript{γ-1100} in Brunauer-Emmett-Teller (BET) values and total pore volume.
Figure S13. Cyclic voltammetric curves at different scan rates (5-100 mV·s⁻¹) for all samples: (a) Zn₇₋₉₀₀, (b) Zn₇₋₁₀₀₀, (c) Zn₇₋₁₁₀₀. 
Figure S14. Galvanostatic charge/discharge curves at different current densities for all samples: (a) Zn\textsubscript{7-900}, (b) Zn\textsubscript{7-1000}, (c) Zn\textsubscript{7-1100}.
Figure S15. The decoupling of capacitance contribution from fast-kinetics processes (yellow) and slow-kinetics processes (orange). (a) Zn$_7$-900, (b) Zn$_7$-1000, (c) Zn$_7$-1100. CVs are collected at scan rate of 100 mV·s$^{-1}$ for all samples.
Table S5. Comparison of supercapacitor performance and BET area of porous carbon for aspyrolysis MOFs or MOFs-derived materials.

| Samples       | MOF precursor | Current density or scan rate | Specific capacitance (F·g⁻¹) | BET (m²·g⁻¹) |
|---------------|---------------|------------------------------|-----------------------------|--------------|
| NPC          | MOF-5[S4]     | 0.25 A·g⁻¹                  | 258                         | 2872         |
| NPC₅₃₀       |               |                              | 158                         | 3040         |
| NPC₆₅₀       |               |                              | 222                         | 1521         |
| NPC₈₀₀       | MOF-5[S5]     | 0.05 A·g⁻¹                  | 151                         | 1141         |
| NPC₉₀₀       |               |                              | 148                         | 1647         |
| NPC₁₀₀₀      |               |                              | 159                         | 2524         |
| MC           |               |                              | 172                         | 1812         |
| MPC          |               |                              | 193                         | 1543         |
| MAC          | MOF-5[S6]     | 0.25 A·g⁻¹                  | 104                         | 384          |
| MC-A         |               |                              | 208                         | 1673         |
| MPC-A        |               |                              | 196                         | 1271         |
| MAC-A        |               |                              | 271                         | 2222         |
| C₈₀₀         |               | 0.25 A·g⁻¹                  | 200                         | 2169         |
| C₁₀₀₀        |               |                              |                             | 3405         |
| Z-8₀₀        | ZIF-8&FA[S7]  | 50 mV·s⁻¹                   | 130                         | 720          |
| Z-9₀₀        |               | 5 mV·s⁻¹                    | 214                         | 1075         |
| Z-1₀₀₀       |               | 50 mV·s⁻¹                   | 112                         | 1110         |
| Nanoporous carbon | ZIF-67[S8]  | 5 mV·s⁻¹                   | 205                         | 350          |
| Nanoporous Co$_3$O$_4$ | 5 mV·s$^{-1}$ | 508 | 148 |
|------------------------|--------------|-----|-----|
| N-PCMPs-A              | ZIF-11$^{[S9]}$ | 1 A·g$^{-1}$ | 307 | 2188 |
| GNRib                  | MOF-74-Rod$^{[S10]}$ | 0.05 A·g$^{-1}$ | 198 | 1492 |
| CNRod                  | MOF-74$^{[S10]}$ | 0.05 A·g$^{-1}$ | 187 | 1559 |
| MPC                    | Zn$_{7+1+1}$$^{[S11]}$ | 0.5 A·g$^{-1}$ | 662 | 1644 |
| 1-900                  | Zn$_7$ | 0.5 A·g$^{-1}$ | 756 | 997.4 |
| Zn$_7$-900             | Zn$_7$ | 1 A·g$^{-1}$ | 1797 | 3119.18 |
| Zn$_7$-1000            | Zn$_7$ | 1 A·g$^{-1}$ | 885 | 876.8 |

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