Electronic Supplementary Information (ESI) for

**In Situ** Formation of Molecular-scale Ordered Polyaniline Film by Zinc Coordination

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Fig. S1 XRD spectra of PANI-Zn varying the ratio between Zn ion and aniline repeating unit of PANI.
Fig. S2 Photograph of the PANI-EB and PANI-Zn films in DMF solvent. The PANI-Zn film exhibited solvent resistance. PANI-Zn film visually had bluish and dark green color due to the weak doping by the coordination with metal ions.
Fig. S3 Raman spectra of PANI-EB and PANI-Zn. The coordination crosslinking affected the Raman spectrum overall, in which most peaks were shifted. Notably, the peak at 1591 cm$^{-1}$ in the PANI-EB spectra indicated C–C stretching of the benzenoid rings.\textsuperscript{1} However, after coordination crosslinking, this peak was shifted to 1576 cm$^{-1}$. Furthermore, the peak at 1354 cm$^{-1}$ from C–N vibrations of the delocalized polaronic structures in PANI-EB was also shifted to 1349 cm$^{-1}$.\textsuperscript{1}
Fig. S4 XPS spectra of C\textsubscript{1s} of PANI and PANI-Zn films. In C\textsubscript{1s} spectrum of PANI-Zn, small shoulder peak at 288.9 eV was observed, which is assumed to be associated with coordinated DMF to Zn\textsuperscript{2+}.
Fig. S5 XPS spectra of Zn$_{2p}$ of PANI-Zn films. The binding energy gap of the spin-orbital photoelectrons between Zn$_{2p3/2}$ and Zn$_{2p1/2}$ is 23.1 eV, related to the coordinated Zn$^{2+}$.\textsuperscript{2}
Fig. S6 XPS spectra of PANI-EB and PANI-Zn films. (a) PANI-EB and (b) PANI-Zn.
Table S1 Compositions of the PANI-EB and PANI-Zn films determined by XPS analysis.

<table>
<thead>
<tr>
<th>Samples</th>
<th>C (%)</th>
<th>O (%)</th>
<th>N (%)</th>
<th>Zn (%)</th>
<th>N/Zn ratio</th>
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<tbody>
<tr>
<td>PANI-EB</td>
<td>70.0</td>
<td>22.3</td>
<td>7.7</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PANI-Zn</td>
<td>65.7</td>
<td>25.6</td>
<td>6.0</td>
<td>2.7</td>
<td>2.2</td>
</tr>
</tbody>
</table>
Fig. S7 Characterization of the crystal structure of PANI-Zn at the molecular scale. (a-c) HRTEM and FFT images of PANI-Zn measured along the [111] direction (a), [112] direction (b) and [114] direction (c). (d) Theoretical electron diffraction patterns of the FCC structure. The measured FFT results correspond to the theoretical patterns of the FCC structure.
Fig. S8 Schematic illustration of the proposed chemical arrangements of PANI-Zn in the [001] plane.
References