On/off switchable electronic conduction in intercalated metal-organic frameworks

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The electrical properties of metal-organic frameworks (MOFs) have attracted attention for MOF as electronic materials. We report on/off switchable electronic conduction behavior with thermal responsiveness in intercalated MOF (iMOF) with layered structure, 2,6-naphthalene dicarboxylate dilithium, which was previously reported as a reversible Li-intercalation electrode material. The I-V response of the intercalated sample, which was prepared using a chemically reductive lithiation agent, exhibits current flow with sufficiently high electronic conductivity, even though it displays insulating characteristics in the pristine state. Calculations of band structure and electron hopping conduction indicate that electronic conduction occurs in the two-dimensional π-stacking naphthalene layers when the band gap is decreased to 0.99 eV and because of the formation of an anisotropic electron hopping conduction pathway by Li intercalation. The structure exhibiting electronic conductivity remains stable up to 200°C and reverts to an insulating structure, without collapsing, at 400°C, offering the potential for a shutdown switch for battery safety during thermal runaway or for heat-responsive on/off switching electronic devices.

INTRODUCTION

The physical properties of several types of metal-organic frameworks (MOFs), which comprise an organic linker and metal ions/clusters, have been studied using tunable and well-defined porous specimens to explore their applicability in gas adsorption and separation (1). Currently, their electrical properties (2–4), such as their conductivity (5–10), magnetism (11, 12), photonic characteristics (13, 14), and energy storage properties (15–18), are also being investigated. Until recently, various kinds of electrically conductive MOFs have been reported: (i) tetraphthalvalene-based MOFs with one-dimensional (1D) π-stacking interaction channels (5, 6), (ii) Ni-dithiolene-based MOFs using p-type semiconductors via a redox mechanism (13), (iii) hexagonally packed dihydroxyterephthalate-based MOFs with 1D charge mobility using metal-oxygen (or metal-sulfur) chains (7–9), (iv) benzentricarboxylate-based MOFs infiltrated with tetracyanoquinodimethane exhibiting tunable electronic conductivity (10), and (v) highly conducting 2D MOFs by stacking sheets with expanded π conjugation (19–21). These electrically conducting MOFs are potential candidates for future models of reconfigurable electronics and sensors. These also could be useful as an alternative approach in organic electronic devices to meet the safety requirements of thermally responsive switching performance at high temperature.

We recently reported the synthesis of intercalated MOF (iMOF) electrode materials through an electrochemically reversible charge transfer Li-intercalation reaction (15–17). As shown in Fig. 1, 2,6-naphthalene dicarboxylate dilithium [2,6-Naph(COOLi)2], a representative iMOF, is composed of aromatic dicarboxylate lithium and forms an organic-inorganic layered structure based on π-stacked naphthalene packing layers and tetrahedral LiO4 units, respectively. It also exhibits two-electron transfer–related reversible intercalation of Li ions, corresponding to a reversible specific capacity of ca. 220 mA·hour g−1, at a constant potential of 0.8 V (versus Li/Li+), without dissolving in the organic electrolyte. This operating potential enables both maintenance of high voltage and suppression of lithium dendrite deposition, generating an internal short circuit for safety issues at the same time (15). Furthermore, 2,6-Naph(COOLi)2 also exhibits another interesting property in that it undergoes a very small change in its unit cell volume (0.33%) while maintaining its framework during Li intercalation. Moreover, the powder of this material, which consists of micrometer-sized white particles, exhibits insulating characteristics. However, the material is electrochemically fully reversible when used to prepare electrodes; this is true even at low carbon content (17). Although there are a number of reports on aromatic dicarboxylate salts that are similar to electrode materials (22–24), these materials have been considered as having poor electronic conductivity, and the essential mechanisms of electronic conduction responsible for the electrochemical reversibility remain to be elucidated. To clarify the reason for the electrochemical reversibility of iMOF electrodes, we performed experimental and theoretical studies of the electrical properties of these electrodes. Our results provide direct evidence for the switching electronic conductivity of 2,6-Naph(COOLi)2 while retaining its ionic conductivity and thermal stability, and suggest that these materials would be highly suited for production of new class of heat-responsive organic switching devices.

RESULTS

We experimentally characterized the electrochemical behavior of 2,6-Naph(COOLi)2 electrodes (fig. S1A). From the discharge curves corresponding to the Li-intercalation reaction, the first discharge potential of these electrodes was found to be ca. 100 mV lower than that during the second and subsequent cycles. As shown in fig. S1B, the differential capacity (dQ/dV) curves exhibited a decrease in polarization with repeated cycling, with the potential change between the first and second discharge cycles being the largest. The current-voltage (I-V) resistance after the second cycle was half the value of the first one (fig. S1B, inset). This suggested that the decrease in the internal resistance is significantly related to Li intercalation, especially during the first cycle, and that the extent of Li intercalation is high enough to change the material from an insulating one to a conducting one.

The detailed Li-intercalation/deintercalation processes of the 2,6-Naph(COOLi)2 electrodes were analyzed using the galvanostatic intermittent titration technique (GITT) to investigate the cause of the internal resistance (fig. S2A). The open circuit potential (OCP) for the initial cycle and that after 10 cycles were almost identical, as shown in fig. S3. What was remarkable was the difference in the polarization...
behavior of $\Delta E_g$ when a current was applied at the OCP (for a detailed explanation, see fig. S2B). The polarization in the initial state (fig. S3A) was twice as large as that after the 10th cycle (fig. S3B). Similarly, the IR drop resistance in the initial state (200 to 300 ohms) (fig. S3A, inset), whose primary component was the electronic resistance from the viewpoint of the time constant, was two to three times larger than that after the 10th cycle (ca. 100 ohms) (fig. S3B, inset). Therefore, it can be concluded that the change in internal resistance contributed to the electronic conduction, which was significantly related to the Li-intercalation state.

Next, we performed simulations using first-principles calculations based on the density functional theory to understand the mechanism of electronic band conduction before and after Li intercalation. We had previously determined two models for the positions of the intercalated Li by x-ray diffraction (XRD) measurement and Rietveld refinement using first-principles calculation (15): In model 1, the intercalated Li ions are located in the vicinity of the tetrahedral LiO$_4$ network layers, whereas in model 2, the main structure is located in the $\pi$-stacked naphthalene layers (fig. S4). In the pristine state (Fig. 2A), the band gap is relatively wide and has an energy ($E_g$) of 3.27 eV. As per models 1 and 2 corresponding to Li intercalation (Fig. 2, B and C, respectively), the Fermi level moves up to the conduction band after Li intercalation, owing to the increase in the electron density because of the organic unit (fig. S5). Therefore, the calculated $E_g$ values for model 1 ($E_g = 1.51$ eV) and model 2 ($E_g = 0.99$ eV) are lower, indicating that Li intercalation transforms 2,6-Naph(COOLi)$_2$ from an insulating material into a semiconducting one; this is especially the case for model 2. Although a 2D channel-type MOF with high conductivity exhibits a low band gap ($E_g = 0.13$ to 0.23 eV) (21), the calculated $E_g$ value for model 2 is relatively lower than the $E_g$ values of previously reported 1D channel-type MOFs, such as cubic arrays of Zn$_4$O(CO$_2$)$_6$-type frameworks ($E_g = 1.3$ to 6.8 eV) (25, 26) or hexagonally packed cylindrical channels of M$_x$O$_y$(CO$_2$)$_z$-type frameworks ($E_g = 1.47$ to 2.60 eV) (9). The CBM of pristine and that of model 1 are linear (red lines in Fig. 2, A and B). On the other hand, the CBM in model 2 is curved and has dispersion (Fig. 2C). This suggests that electrons in conduction band in model 2 are delocalized and that electronic mobility increases. The calculated 2D and 3D electron density distributions of the CBM indicated the following: The pristine structure is localized intramolecularly along the cross-sectional direction of the $\pi$-stacked naphthalene packing layers (Fig. 2, D and G). In contrast, in the case of model 1, the Li-intercalated structure is delocalized intramolecularly between C1 and C1’ (Fig. 2, E and H). As per model 2, it is delocalized intermolecularly between C1 and C2 (or C1’ and C2’), in addition to being intramolecularly delocalized (Fig. 2, F and I). This reveals that, in model 2, Li intercalation provides an electron hopping conduction path via the 2D $\pi$-stacked naphthalene packing organic layers.

To further investigate electron conduction between adjacent molecules, the hopping conduction parameters, including the transfer integral ($V$), diffusion coefficient ($D$), and drift mobility of hopping ($\mu_D$), for the pristine structure and the Li-intercalated one corresponding to model 2 were determined on the basis of the Marcus theory (for a detailed explanation, see Materials and Methods) (27). To be able to describe hopping transport before and after the Li intercalation of the 2,6-Naph(COOLi)$_2$ crystal, we considered the following three hopping pathways corresponding to the Li-intercalation state (Fig. 2, D and G): (i) $\pi$-conjugated molecules arranged in a layered basal herringbone packing structure (P), (ii) basal-edge packing (T), and (iii) edge-edge packing across the tetrahedral LiO$_4$ layer (L). The transfer integrals of all three hopping pathways corresponding to the Li-intercalation state were larger than those before Li intercalation, as shown in Fig. 3C. In contrast, the diffusion coefficient (Fig. 3D) and drift mobility of hopping (Fig. 3E) for path T increased markedly, by three orders of magnitude, after Li intercalation. Furthermore, those for path P exhibited high values, whereas those for path L decreased in value. These results suggest that anisotropic electron hopping conduction occurs in the $\pi$-stacked naphthalene packing layer along the $b$-$c$ planar direction but not in the organic-inorganic stacking layer along the $b$-$c$ vertical direction; this gives rise to anisotropic 2D electronic transport within the organic layer of the 2,6-Naph(COOLi)$_2$ crystal. Moreover, these results agree with the calculated electron density distribution of the band structure, as shown in Fig. 2. The hopping conduction calculations performed in this work can be used as a molecular design tool to find high-electron conduction IMOF materials.

To gather direct evidence for electronic conduction in 2,6-Naph(COOLi)$_2$, a Li-intercalated sample was prepared using lithium naphthalenide, which is a known reductive lithiation agent (28, 29), and electronic conductivity measurements were performed on the
synthesized sample. With the reductive lithiation agent and composite electrode sample of conducting carbon free (see Fig. 4A), a Li-intercalated sample could be prepared without having to use any electrochemical techniques. The sample changed from white in the pristine state to black in the Li-intercalated state (Fig. 4B). Furthermore, the XRD patterns corresponding to the pristine and Li-intercalation states were different and confirmed that the respective crystal structures of the samples were similar to those reported previously (fig. S6) (15). This confirmed that naphthalene-catalyzed reductive lithiation can be used to induce the Li-intercalated state in 2,6-Naph(COOLi)₂, which is black in this state. Although exfoliation occurs when naphthalene is incorporated in the interlayer when other layered materials, such as graphite (29) and chalcogenides (30), are made to react with lithium naphthalenide, the reaction of 2,6-Naph(COOLi)₂ and lithium naphthalenide did not cause the exfoliation of the crystal structure, which resulted in amorphous naphthalene.

The I-V curves of the electrodes of the Li-intercalated sample using closed parallel-electrode cell (fig. S7) were linear, as shown in Fig. 4C, indicating that the Li-intercalated sample exhibited a favorable current response at an applied bias voltage of 0.5 V; in contrast, in the pristine

![Fig. 2. Predictive calculation of electronic band conduction. (A to C) Calculated electronic band structures obtained from the HSE06 functional for the pristine sample (A) and the Li-intercalated sample corresponding to model 1 (B) and model 2 (C). The valance band maximum and conduction band minimum (CBM) are represented in the band structures as blue and red lines, respectively. (D to F) 3D electron density distribution (obtained with the PBEsol functional) of the CBM of the 2,6-Naph(COOLi)₂ crystal structure for the pristine sample (D) and the Li-intercalated sample corresponding to model 1 (E) and model 2 (F). Orange, intercalated Li; green, pristine Li; red, O; blue, C; white, H. (G to I) 2D electron density distribution of the CBM across the π-stacking packing naphthalene layer via the C₁, C₁', C₂, and C₂' carbons corresponding to the figure above for the pristine sample (G) and the Li-intercalated sample obtained using model 1 (H) and model 2 (I).](http://advances.sciencemag.org/)

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state, the sample exhibited a negligible current response. To investigate the detailed electrical characteristics, we performed electrochemical impedance spectroscopy (EIS) using the same cell. In the Bode plots shown in Fig. 4D, the Li-intercalated sample showed ca. 10^5 ohms. This value is four orders of magnitude lower than that of the pristine sample (ca. 10^9 ohms), as the frequency becomes lower. In the Nyquist plots shown in Fig. 4E, blocking behavior corresponding only to ionic conduction without electronic conduction was observed in the pristine sample, which denotes a mixed electronic and ionic conduction (fig. S8) (31–33). Because the low-frequency resistance component of the Li-intercalated sample corresponds to an electronic resistance (R_e), the observed current response of the Li-intercalated sample shown in Fig. 4C is due to a decrease in the R_e, suggesting that a switchable electronic conduction path is formed by the Li intercalation of 2,6-Naph(COOLi)_2. In the states with white and black colors (Fig. 4B), 2,6-Naph(COOLi)_2 exhibited insulating and conducting characteristics, respectively. The results of inductively coupled plasma optical emission spectroscopy (ICP-OES) showed that the quantity of the intercalated Li can be controlled by the treatment time with lithium naphthalenide; in addition, electronic conductivity was improved depending on the quantity of the intercalated Li (fig. S9).

![Fig. 3. Predictive calculation of electron hopping conduction. (A and B) Schemes of electron hopping pathways between adjacent molecules for the pristine sample (A) and the Li-intercalated samples corresponding to model 2 (B). Orange, intercalated Li; green, pristine Li; red, O; blue, C; white, H. (C to E) Comparison of the predicted electronic transfer integral (C), diffusion coefficient (D), and drift mobility of hopping (E) before and after Li intercalation.](image)

![Fig. 4. Experimental confirmation of switchable electronic conduction. (A) Schematic of chemical reductive lithiation of 2,6-Naph(COOLi)_2 using lithium naphthalenide. (B) Photographs of 2,6-Naph(COOLi)_2 electrode without conductive carbon before (left) and after (right) being immersed in a lithium naphthalenide/tetrahydrofuran (THF) solution. (C to E) Comparison of I-V curves (C), Bode plots (D), and Nyquist plots (E) for 2,6-Naph(COOLi)_2 samples before (blue) and after (red) being immersed in the same solution. In (E), the inset is the equivalent circuit for a mixed electronic and ionic conductive material. The intersections at high (100 kHz) and low (1 Hz) frequencies with the real axis are the mixed electronic and ionic resistances in parallel (R_e + R_i) and the only electronic resistance (R_e), respectively. (F) Arrhenius plots of each conductivity obtained from I-V curves and EIS at various temperatures (fig. S10), \( \sigma_e \) (red) and \( \sigma_i \) (green), which are calculated using the equivalent circuit model shown in the inset of (E) for the mixed electronic and ionic conductive material, and polarization measurement, \( \sigma_{\text{pol}} \) (blue). All conductivity values were calculated using percolation theory (see Materials and Methods).](image)
Both the $I$-$V$ curves and Nyquist plots of the Li-intercalated sample showed lower resistance behavior as the temperature increased (fig. S10). The Nyquist plots of the Li-intercalated sample showed depressed semicircle at all temperatures. The bulk electronic conductivity ($\sigma_e$) and ionic conductivity ($\sigma_i$) were calculated separately from Nyquist plots of highest and lowest values using the equivalent circuit model for mixed electronic and ionic conductors (fig. S8B). The obtained $\sigma_e$ and $\sigma_i$ were $10^{-6}$ to $10^{-5}$ S cm$^{-1}$ and $10^{-8}$ to $10^{-7}$ S cm$^{-1}$ within a temperature range of 25° to 60°C, respectively. The $\sigma_i$ agrees with that calculated from the $I$-$V$ curves ($\sigma_{I-V}$). The obtained $\sigma_i$ is comparable to the conducting MOFs, such as hexagonally packed cylindrical channels of M$_2$O$_3$(CO$_2$)$_3$-type frameworks ($10^{-6}$ to $10^{-5}$ S cm$^{-1}$) (9), tetrathiafulvalene-based frameworks ($10^{-6}$ to $10^{-4}$ S cm$^{-1}$) (6), tetracyanoquinodimethane-based frameworks ($10^{-5}$ to $10^{-3}$ S cm$^{-1}$) (34), and dithiolene-based frameworks ($10^{-1}$ to $10^{-3}$ S cm$^{-1}$) (13). In addition, compared with $\sigma_e$ ($10^{-5}$ to $10^{-4}$ S cm$^{-1}$) and $\sigma_i$ ($10^{-5}$ to $10^{-3}$ S cm$^{-1}$) of pristine oxide-based electrode materials for batteries, which are known as mixed electronic and ionic conductors (33, 35, 36), the proposed material has comparable electronic and ionic conductivities. Both $\sigma_e$ and $\sigma_i$ display Arrhenius behavior (Fig. 4F). The activation energies ($E_a$) for $\sigma_e$ and $\sigma_i$ calculated from Arrhenius plots are ca. 18.3 kJ mol$^{-1}$ (or ca. 190 meV) and ca. 3.5 kJ mol$^{-1}$ (or ca. 36 meV), respectively. Although the $E_a$ for $\sigma_i$ is slightly larger than that in the previous reports of high-mobility conducting MOF materials (10, 20), this value is one order of magnitude smaller than that of the pristine electrode materials (36, 37). The $E_a$ for $\sigma_i$ was lower than that of the ionic conductors of well-known solid electrolytes (38–40). The low $E_a$ ensures the least fluctuation of ionic conductivity and therefore favors the practical applications in a broad operating temperature range.

When the sample was used as an electrode material, the disappearance of its electronic conductivity during elevated temperature process at approximately 200°C was expected to act as a shutdown switch for battery safety, because its insulating nature would increase safety during thermal runaway. To verify this phenomenon, we measured the XRD patterns of the Li-intercalated sample obtained during heating (Fig. 5A). The results showed that the crystal structure exhibiting electronic conductivity remains intact until approximately 180°C. Thereafter, the crystal structure changed to the initial one (blue pattern in fig. S6) exhibiting insulating characteristics via a two-phase coexistence region in a temperature range of 180° to 250°C, where the initial structure with insulating property was maintained until a temperature of 400°C. In addition, direct evidence of disappearance of electronic conductivity above 200°C was given by EIS and $I$-$V$ curve of Li-intercalated sample after heating (Fig. 5, B to D). In the heating sample at 100°C, which keeps the Li-intercalated crystal state, although slight resistance increase was confirmed at a low frequency from the Bode plots (Fig. 5B), the current response was observed from the $I$-$V$ curve (Fig. 5C). In the Nyquist plot, a new semicircle appeared in the low-frequency range (Fig. 5D). This indicates the presence of a grain-boundary resistance by growth of the Li-containing film, which was formed during the

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**Fig. 5. Heat-responsive on/off switching of electronic transport characteristics.** (A) Temperature dependence of in situ powder XRD patterns of Li-intercalated 2,6-Naph(COOLi)$_2$ for temperatures of up to 400°C. (B to D) Change in Bode plots (B), $I$-$V$ curves (C), and Nyquist plots (D) for pristine, Li-intercalated samples and Li-intercalated samples prepared by heat treatment at temperatures of 100° and 200°C.
The equivalent circuit of this Nyquist plot can be explained in fig. S8C (32). There is almost no change in bulk electronic resistance while generating grain-boundary resistance in the sample heated at 100°C. In contrast, in the heating sample at 200°C, which returns to the initial crystal state, from the impedance behavior, the electronic resistance increase was confirmed and the current response of the I-V curve drastically disappeared.

To investigate the Li that disappeared from the main structure during heat treatment, we compared the XRD patterns of pristine nondoped sample and Li-doped sample after heating, as shown in fig. S11. In the Li-intercalated sample after heating, several new peaks corresponding to LiO, Li₂O, Li₃O H₂O, and Li₂CO₃ appeared in the high-angle region. These peaks appeared from temperatures higher than 200°C corresponding to the start of the Li release (fig. S12). These are Li-containing components that become resistant phase. Therefore, the XRD results imply that the Li released from the Li-doped sample during heating is incorporated into the Li-containing components and becomes a grain-boundary resistance component. In addition, in the Li-intercalated sample after heating, although the (011) reflection corresponding to the inorganic tetrahedral LiO₄ network (16) did not change, the (102) reflection corresponding to the π-stacked naphthalene packing layer shifted to the lower angle. This result means the expansion of the π-stack distance of naphthalene and thus the inhibition of the hopping conduction of the main structure. Therefore, the heat treatment of the Li-doped sample includes the following three-electron conduction blocking mechanisms: (i) the disappearance of the main crystal structure responsible for hopping conduction accompanying Li release, (ii) the inhibition of hopping conduction accompanying the spreading of stacked naphthalene distance in the main crystal structure, and (iii) the formation of Li-containing insulating layer with the released Li and heating at the grain boundary. This electronic conduction blocking mechanism will be a useful shutdown function during thermal runaway. Although there are many indirect approaches to battery safety using electrolyte (41, 42), separators (43), and peripheral materials (44, 45), the proposed material is regarded as a direct approach to the safety of the electrode that stores electrical energy.

**DISCUSSION**

This study is the first to provide theoretical and experimental evidence for mixed electronic and ionic conductivity induced in electrode materials based on aromatic dicarboxylate salts such that the materials exhibit a reversible redox response and should facilitate the development of MOFs that exhibit switchable anisotropic electronic conduction. Although the electronic conduction observed in previously reported MOF materials has been attributed to metal-metal or metal-ligand interactions (2–4, 7–10, 12, 18), our results demonstrate hopping conduction in an iMOF material based on ligand-ligand interactions between the π-stacking aromatic units owing to reductive lithium doping; the organic framework design will be the key to improving the electronic conductivity.

The mechanism of electronic conduction triggered by Li intercalation while keeping ionic conductivity is such that it allows for electrochemical reversibility and can be exploited to fabricate low-resistance electrodes for batteries and supercapacitors that exhibit high-power performances. We also envisage that the switchable electronic conduction/insulation properties of this Li-doped iMOF at approximately 200°C will be exploited to fabricate heat-responsive on/off switching electronic devices, such as battery electrode with shutdown function or organic transistors for producing current interrupters that improve safety. To achieve organic transistors, technology of pellets and thin-film fabrication with excellent responsiveness using the proposed material would be necessary.

**MATERIALS AND METHODS**

**Sample synthesis**

The synthesis of 2,6-Naph(COOLi)₂ was reported previously (15). 2,6-Naph(COOLi)₂ was synthesized from lithium hydroxide monohydrate (4.85 g, 115.6 mmol) and 2,6-naphthalenedicarboxylic acid (10.0 g, 46.3 mmol) by heating using reflux in 300 ml of methanol. The solution was initially clear; however, a white precipitate formed over the course of 30 min. The suspension was stirred under the reflux conditions for 12 hours. The liquid in the suspension was evaporated, and the resulting solid was washed with methanol and dried under ambient conditions. The product obtained was in the form of needle-shaped white crystals [96.8% yield based on 2,6-Naph(COOLi)₂].

**Chemical Li intercalation**

A lithium naphthalenide solution (0.1 mol dm⁻³) was prepared using a previously described procedure (28, 29). Naphthalene was dissolved in anhydrous THF to prepare a 0.1 M solution, and an equimolar amount of lithium was added to the 0.1 M naphthalene solution under stirring at room temperature in an Ar-filled glove box. The solution turned dark green after the addition of lithium. The quantity of Li element in the pristine and reduced samples was confirmed by ICP-OES (CIROS 120EOP, Rigaku and SPECTRO).

**In situ powder XRD**

The XRD pattern of the Li-intercalated 2,6-Naph(COOLi)₂ sample free of conductive carbon was obtained using a Debye-Scherrer camera at the BLS2 beamline, Aichi Synchrotron Radiation Center, Aichi prefecture, Japan (proposal no. 201601031). The data were recorded with a PILATUS 100K detector (DECTRIS Ltd.) with a resolution of 1.00011 Å (calibrated using standard CeO₂ powder) for 2θ values of 10° to 24°; the step size was 0.01°. The sample was heated with a high-temperature N₂ gas blower at a rate of 5°C min⁻¹ to temperatures of up to 400°C, and the XRD pattern was recorded every 10°C after a wait time of 2 min for each temperature. Before the in situ XRD measurements, the Li-intercalated 2,6-Naph(COOLi)₂ sample was prepared by soaking the 2,6-Naph(COOLi)₂ electrode free of conductive carbon in the lithium naphthalenide/THF solution (0.1 mol dm⁻³) in an Ar-filled glove box. The 2,6-Naph(COOLi)₂ electrodes free of carbon as a conductive agent were also prepared by dispersing 98 weight % (wt %) 2,6-Naph(COOLi)₂ and 2 wt % carboxymethylcellulose (CMC) in water and then by coating the slurry on a Cu foil; the electrode loading rate was ca. 3 mg cm⁻². After the electrode had been prepared, the sample was removed from the electrode, placed in a capillary tube, and sealed to prevent oxidation by moist air during the XRD measurements, which were performed in an Ar-filled glove box.

**Electrochemical measurements**

The galvanostatic charge/discharge and GITT measurements were performed using a two-electrode system of Li/2,6-Naph(COOLi)₂ cells...
assembled in an Ar-filled glove box. The 2,6-Naph(COOLi)₂ electrodes were prepared by coating a dispersion of 81 wt % 2,6-Naph(COOLi)₂, 14 wt % carbon black as a conductive agent, 2 wt % CMC as the binder, and 3 wt % styrene butadiene rubber (also used as a binder) in water on a Cu foil. The electrode loading rate was ca. 3 mg cm⁻². The electrolyte used was 1 M LiPF₆ dissolved in a solution of ethylene carbonate, dimethyl carbonate, and ethyl methyl carbonate (volume ratio of 30:40:30). A microporous polypropylene film was used as the separator. During the galvanostatic charge/discharge measurements to determine the specific capacity and electrochemical reversibility of the 2,6-Naph(COOLi)₂ electrodes at 25°C, coin-type cells were cycled between 0.5 and 2.0 V (versus Li/Li⁺) at a rate corresponding to the full charging to the theoretical capacity of 2,6-Naph(COOLi)₂ per 10 hours.

Electrical measurements
All electronic transport characteristics were performed using closed parallel-electrode cell with a four-electrode system (12962A, Solartron). Cell resistance without sample is smaller by seven to eight orders of magnitude when compared to cell with sample and can therefore be ignored. The I-V characteristics and EIS were measured at 25°C with a Solartron MultiStat system (1470E, Solartron) using 2,6-Naph(COOLi)₂ electrodes free of conductive carbon; the measurements were made both before and after the electrodes were immersed in the lithium naphthalenide/THF solution. After the removal of the immersed solution, the electrode was washed with THF. Before measurement, the electrodes were dried. The closed parallel-pellet cells were then prepared with electrodes in a dry state (fig. S7). The electrical connection was formed using a piece of Cu foil. The I-V curves were measured at a scan rate of 100 mV s⁻¹ within the polarization range of −0.5 to 0.5 V using a two-electrode system assembled in an Ar-filled glove box. EIS measurements of the same cell were performed at OCP. The frequency was varied from 100 kHz to 1 Hz with a perturbation amplitude of 0.5 V (peak to peak). The measurements were performed between −30° and 60°C. Before the measurement of the heat treatment samples, the Li-intercalated sample was annealed at temperatures of 100° and 200°C for 5 min under Ar atmosphere.

Percolation theory in electronic properties
The effective electronic conductivity (σ_eff) of conductor-insulator composites is defined as follows

$$\sigma_{\text{eff}} = \frac{1}{R_s S} \frac{L}{p c}$$  (1)

where $R_s$, $L$, and $S$ are resistance, composite electrode thickness, and electrode geometric area, respectively. The actual conductivity can be estimated from percolation theory (46–48). According to the percolation theory, the effective electronic conductivity (σ_eff) of conductor-insulator composites can be expressed as follows

$$\sigma_{\text{eff}} = \sigma_0 (p - p_c)^n$$  (2)

where $\sigma_0$ is the actual conductivity, $p$ is the weight fraction of the conductive material, $p_c$ is the critical weight fraction at percolation threshold, and $n$ is the critical exponent that depends on the topological dimensionality of the percolating system. The $p$ value of this composite electrode in this study is calculated to be ca. 0.466. The $p_c$ value of the conductor-insulator composites is reported as 0.32 (49, 50). In the case of random void model, in which insulating penetrable spheres are randomly immersed in a conducting continuum, the exponent of $n$ is found to be 2.38 (49).

Kinetic interpretation of individual conductivities of Li-intercalated 2,6-Naph(COOLi)₂ composite electrodes
To determine the kinetic parameters of the composite electrodes, the activation energies of each conductivity were evaluated using the Arrhenius equation

$$\sigma = A \exp\left(-\frac{E_a}{RT}\right)$$  (3)

where $A$, $E_a$, $R$, and $T$ are the frequency factor, activation energy, gas constant, and absolute temperature, respectively.

Calculation of electronic band structure and density of states
First-principles calculations for structural optimization and analysis of the electronic properties were performed with the Vienna ab initio simulation package (51) using the projector-augmented wave method. The cutoff points for the kinetic energy and $k$-point spacing were set to 500 eV and approximately 0.1 Å⁻¹, respectively. During the optimization of the crystal structures, Gaussian smearing with a width of 0.2 eV was adopted for the integral over the Brillouin zone. For the exchange-correlation energy within the density functional theory, the PBEsol functional (52), which revises the Perdew-Burke-Ernzerhof–generalized gradient approximation functional to improve the equilibrium properties of solids and surfaces, was applied. For the electronic structure calculations, the tetrahedron method with Blöchl corrections and the HSE06 functional (53, 54) were used for the integral over the Brillouin zone and the exchange-correlation energy, respectively.

Calculation of electron hopping conduction using Marcus theory
The Marcus theory was widely used to calculate the hopping mobility in organic semiconductors (27, 55, 56). The electron hopping rate between neighboring molecules ($W$) can be determined on the basis of the Marcus theory as shown

$$W = \frac{V^2}{\hbar} \left(\frac{\pi \lambda}{\lambda k_B T}\right)^{1/2} \exp\left(-\frac{\lambda}{4 k_B T}\right)$$  (4)

where $V$ is the transfer integral between the initial and final states (in electron volts), $\lambda$ is the reorganization energy (which is defined as the energy change associated with the geometry relaxation during charge transfer), $\hbar$ is Plank’s constant, and $k_B$ is the Boltzmann constant. The diffusion coefficient ($D$) is calculated from the hopping rates (cm² s⁻¹) as

$$D = \frac{1}{2n} \sum_i r_i^2 W_i P_i$$  (5)

where $n$ is the dimensionality, $i$ represents a specific hopping pathway, $r_i$ is the hopping distance between two molecules, and $P_i$ is the
hopping mobility, which is calculated by

$$ P_i = \frac{W_i}{\sum W_i} \quad (6) $$

The drift mobility of hopping ($\mu_h$) can then be evaluated from the Einstein relation ($cm^2 V^{-1} s^{-1}$)

$$ \mu_h = \frac{e}{k_B T} D \quad (7) $$

where $e$ is the electronic charge.

The transfer integral ($V$) was calculated using the site-energy correction method (57) and the DiPro approach (58). The reorganization energy ($\lambda$) was obtained from the sum of the following two energy differences (56)

$$ \lambda = \lambda_1 + \lambda_2 \quad (8) $$

$$ \lambda_1 = E_{eig0} - E_{eig}^* \quad (9) $$

$$ \lambda_2 = E_{eig}^0 - E_{eig0} \quad (10) $$

where $E_{eig}^*$ ($E_{eig}$) is the energy of a charged molecule in the equilibrium neutral (charged) geometry and $E_{eig0}$ ($E_{eig}^0$) is that of a neutral molecule in the equilibrium neutral (charged) geometry. The calculations for the transfer integral and reorganization energy were performed using the Gaussian 09 package (59), with the B3LYP functional and the 6-311++G basis set for C12H6O4Li2(Li2) molecules extracted from the experimental crystal structure.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/8/e1603103/DC1

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On/off switchable electronic conduction in intercalated metal-organic frameworks
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