

## **Electronic Supplementary Information (ESI)**

# **Prolonging the n-type conduction of thermoelectric carbon nanotubes exposed to warm air by mixing hydrated water into the adsorbed dopant layers composed of Li<sup>+</sup>-receptor molecules**

Shinichi Hata,\*<sup>a</sup> Chika Nakagawa,<sup>b</sup> Ayako Taketoshi,<sup>c</sup> Toru Murayama,<sup>a,d</sup> Tamao Ishida,<sup>a</sup>  
Yukou Du,<sup>e</sup> Yukihide Shiraishi\*<sup>b</sup> and Naoki Toshima<sup>b,f</sup>

<sup>a</sup> Department of Applied Chemistry for Environment, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, 1-1 Minami-osawa, Hachioji, Tokyo 192-0397, Japan

<sup>b</sup> Department of Applied Chemistry, Faculty of Engineering, Sanyo-Onoda City University, Daigaku-dori, 1-1-1, Sanyo-Onoda, Yamaguchi 756-0884, Japan

<sup>c</sup> Department of Advanced Materials Chemistry, Graduate School of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

<sup>d</sup> Yantai Key Laboratory of Gold Catalysis and Engineering, Shandong Applied Research Center of Gold Nanotechnology (AU-SDARC), School of Chemistry & Chemical Engineering, Yantai University, 30 Qingquan Road, Yantai 264005, China

<sup>e</sup> College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China

<sup>f</sup> Tokyo University of Science Yamaguchi, Japan

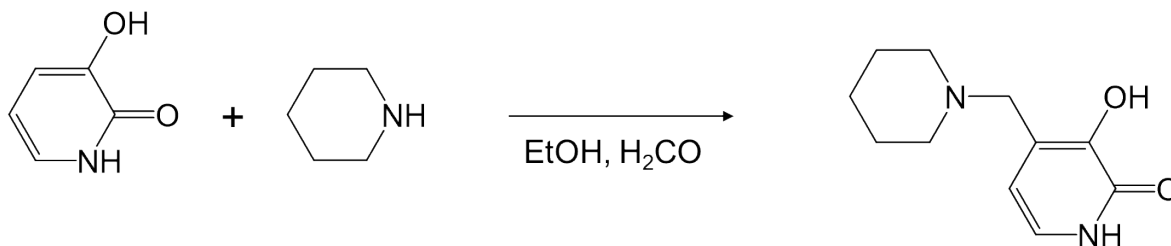
\*Corresponding authors: Email: [sinhata@tmu.ac.jp](mailto:sinhata@tmu.ac.jp) (S.H.); [shiraishi@rs.socu.ac.jp](mailto:shiraishi@rs.socu.ac.jp) (Y.S.)

## EXPERIMENTAL SECTION

### Materials

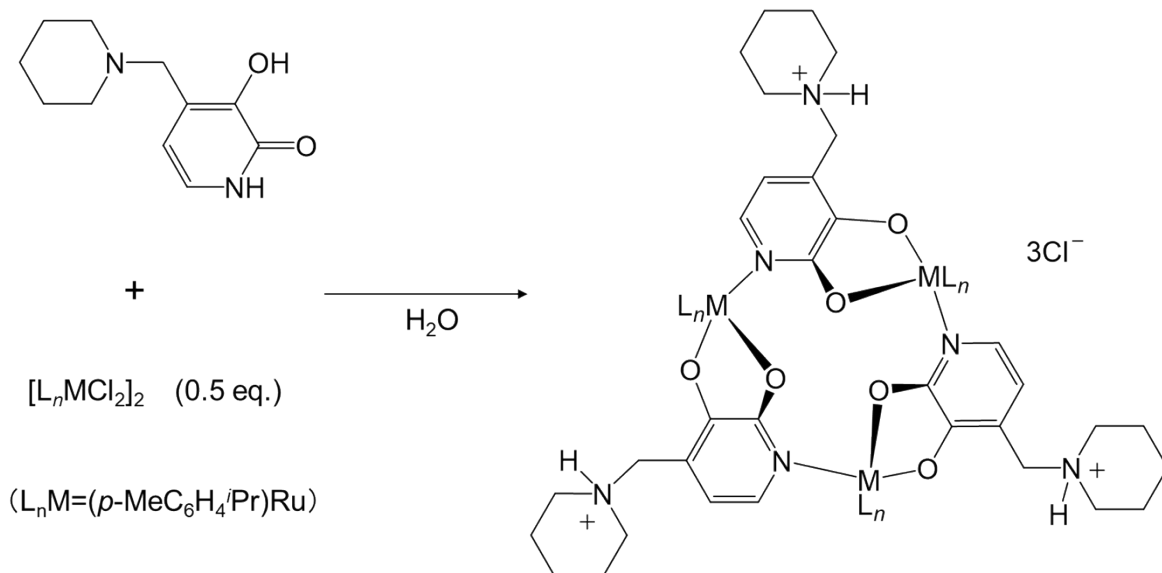
Single-walled carbon nanotubes (CNTs) (Product ID EC 1.5, purity > 90%, diameter:  $1.5 \pm 0.8$  nm, metal/semiconductor composition = 1:2) were obtained from Meijo Nano Carbon Co. Ltd., Aichi, Japan. Piperidine, dichloro(p-cymene)ruthenium(II) dimer, formaldehyde, ethanol, acetone, and lithium chloride were purchased from FUJIFILM Wako Pure Chemical, Japan. 2,3-Pyridinediol was obtained from Kanto Chemical Co., Inc., Japan. All materials were used as received without further purification. Ultrapure water (specific resistance of  $18.2 \text{ M}\Omega \text{ cm}$  at 298 K) was used in all experiments. The polyimide films were supplied by UBE Industries, Ltd., Japan.

### Synthesis



Scheme 1. Transformation of 2,3-dihydroxypyridine to Compound 1

**3-Hydroxy-4-piperidino-methyl-2-(1H)-pyridinone (1).** The title compound was synthesized by a modified version of a procedure reported in the literature, as described below.<sup>1</sup> In a 100 mL two-necked eggplant flask, 1.0 g of 2,3-dihydroxypyridine and 19 mL of ethanol were weighed, and a stirrer tip was placed into the solution. The solution was stirred at room temperature for 30 min, and 0.7 mL of formaldehyde, 1.57 g of piperidine, and 1.0 mL of ethanol were then added, followed by stirring in an oil bath at 323 K for 12 h. After the reaction, the solvent was removed using a rotary evaporator to obtain the crude product. In this product, 15 mL of acetone and 15 mL of ethanol were added, and the mixture was dispersed in an ultrasonic bath for 10 min; it was then allowed to stand in ice water for 10 min. After spontaneous filtration, the product, 3-hydroxy-4-piperidinomethyl-2-(1H)-pyridinone, was dried in a vacuum dryer for 30 min. The yield was 94%. Their identities were confirmed by <sup>1</sup>H nuclear magnetic resonance (NMR) spectroscopy, as reported previously.<sup>1</sup>



Scheme 2. Transformation of Compound 1 to Receptor

**Receptor.** The compound was synthesized according to a modified version of a procedure reported in the literature described below.<sup>2</sup> In a 200 mL Erlenmeyer flask containing dichloro(*p*-cymene)ruthenium(II) dimer (0.68893 g, 1.125 mmol) 468.58 mg of compound 1, 150 mL water, and a stirrer tip were added. This was heated to 313 K and stirred until a clear solution was obtained. After stirring at 313 K for another 12 h, the solvent and other components of this solution were concentrated in a rotary evaporator until the liquid volume in the vessel was reduced to 10 mL. The solution was transferred to a Teflon Petri dish and dried on a hot plate at 363 K for 12 h to obtain a brown powder (95% yield). Their identities were confirmed by <sup>1</sup>H NMR spectroscopy, as reported previously.<sup>2</sup>

#### Fabrication of the Li<sup>+</sup>-receptor/CNT films in an aqueous medium

A Li<sup>+</sup>-receptor/CNT film was prepared as follows. First, a 3.0 mM aqueous Li<sup>+</sup>-receptor solution, which was prepared by admixing the respective aqueous receptor solution with an aqueous lithium chloride solution, was used as a dispersant for the nanotubes. In a 13.5 mL screw tube, 6.0 mg of CNTs was added to 6.0 mL of the 3.0 mM aqueous Li<sup>+</sup>-receptor solution; subsequently, the mixture was stirred with an ultrasonic homogenizer (Ultrasonic Cleaner, TAITEC; Branson Sonifier 250D, Central Scientific, Tokyo, Japan) for 5 min while cooling in an ice bath, as the reaction was exothermic. The homogenized CNT solution (3.0 mL) was drop-cast onto a polyimide sheet (5 × 3 cm) and placed on a hot plate at 333 K for 1 h. To improve film formation, another 2.0 mL of the homogeneous CNT solution was cast on top of the original film and dried at 333 K for 5 h and at 383 K for 30 min to produce a dry Li<sup>+</sup>-receptor/CNT film. For comparison, CNT films without dopant (pure CNTs) were also prepared. The films were cut into samples with dimensions of 4 mm × 16 mm for TE measurements. The receptor/CNT films were prepared similarly.

### **Characterization**

The various CNT films were stored in a typical drying chamber under the ambient atmosphere, and their TE properties and structures were evaluated. The thickness of the fabricated film was measured five times at different locations using a thickness meter (LGK-0110, Mitutoyo Corporation, Japan), and the average thickness was calculated. The CNT composite layer on the polyimide sheet was  $5.0 \pm 1.0$  μm thick. Notably, the prepared film had a thickness > 100 nm, and its TE performance was observed to be independent of the thickness of the CNT film.<sup>3</sup> The in-plane TE properties of the TE conversion films were

quantified using a commercial ZEM-3 M8 instrument (ULVAC-RIKO Inc., Japan) purged with He gas. All samples were pretreated by heating them to 370 K, and the measurements were performed at least three times at 345 K. The conversion efficiency of the corresponding material can be estimated using the thermal power factor (PF).

$$\text{PF} = S^2 \sigma, \quad (1)$$

where  $S$  is the Seebeck coefficient ( $S > 0$  and  $S < 0$  for p-type and n-type semiconductors, respectively), and  $\sigma$  is the electrical conductivity.

For accelerated degradation testing, the unlaminated films were placed on an uncovered glass slide and stored in an LC-222 box blower (ESPEC CORP., Japan) at 373 K and 48% relative humidity. For the transient TE measurements, the sample was stored in this box blower at all times except when measurements were being performed.

The CNT films were observed by field-emission scanning electron microscopy (SEM) (S-4800 Type2, Hitachi, Japan) at an accelerating voltage of 25 kV. For the SEM observations, each film sample was fixed to the sample holder using carbon tape, and the samples were observed without using any coating processes (such as vapor deposition). The average bundle diameters and standard deviations were calculated by measuring the diameters of 200 CNT bundles in enlarged SEM images. Scanning transmission electron microscopy (STEM) images were obtained using a JEM-ARM200F (JEOL Ltd.) electron microscope equipped with an energy-dispersive X-ray spectrometer at an accelerating voltage of 100 kV. Raman spectra were obtained using an NRS-7100 laser Raman spectrometer (JASCO, Japan) with a 532 nm green line laser at room temperature in the ranges of 120–240  $\text{cm}^{-1}$  and 1500–1640  $\text{cm}^{-1}$ . The  $\text{N}_2$  adsorption isotherms at 77 K and  $\text{H}_2\text{O}$  adsorption isotherms at 303 K were

measured using a BELSORP-max instrument (MicrotracBEL, Japan). Before each sorption measurement, all samples were activated by heating to 378 K under reduced pressure ( $<10^{-2}$  Pa) for 12 h. Thermogravimetric analysis (TGA) was performed using a TG/DTA7200 instrument (HITACHI) between 323 and 523 K at  $10\text{ K min}^{-1}$  using 5–6 mg of sample in an Al crucible in the presence of flowing  $\text{N}_2$  at  $150\text{ mL min}^{-1}$ . In the TGA test, the inlet gas was  $\text{N}_2$ . Because it was difficult to peel the CNT film from the polyimide sheet, a CNT-independent sheet without support (prepared on a polytetrafluoroethylene petri dish) was used for gas-adsorption measurements and TGA. Films were prepared as described above, and samples with film thickness errors  $\leq \pm 1.0\ \mu\text{m}$  were obtained.

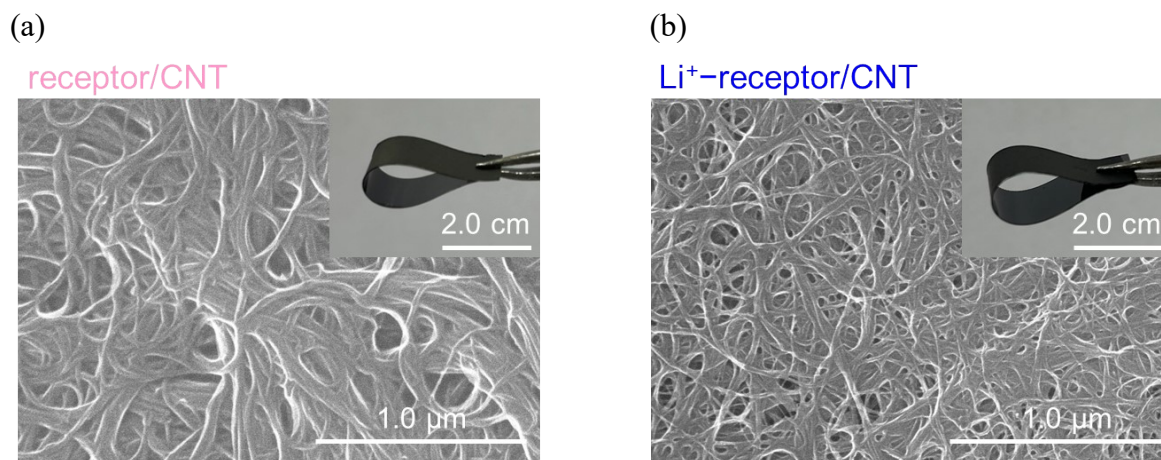


Fig. S1 Scanning electron microscopy surface images of (a) receptor/Carbon nanotube (CNT) and (b)  $\text{Li}^+$ -receptor/CNT films; insets: macroscale photographs of the entire film.

In addition to the identifiable fibrous CNTs, the STEM images (Figures S2 and S3) of the  $\text{Li}^+$ -receptor/CNT reveal numerous bright spots on the CNT surface. These objects range in size from 0.1 to 0.2 nm and correspond to a single atom. Considering the difference in contrast between these spots and the CNT in the image, these spots may indicate Ru atoms, which have a larger atomic number than C and make up the receptor molecule. Furthermore, EDX analysis of the outer wall of the CNT bundle shows that C and Ru atoms are uniformly distributed without no local concentrations, indicating that the distribution of Ru is not related to the presence of C. In addition, signals originating from N atoms (which constitute dopants) were also detected. Although we were unable to identify Li, which is a very light atom, the atomically dispersed Ru provided important evidence that the dopant molecules used as dispersants neatly covered the CNT bundle surface.

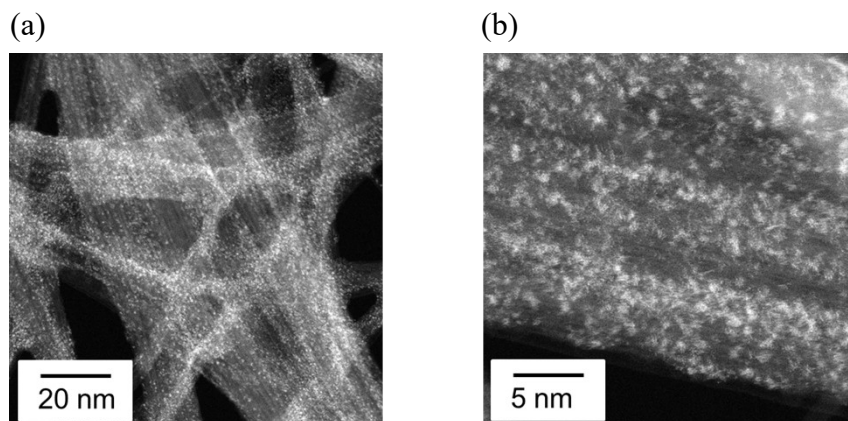


Fig. S2. (a) Low- and (b) high-magnification scanning transmission electron microscopy (STEM) images of  $\text{Li}^+$ -receptor/CNTs.



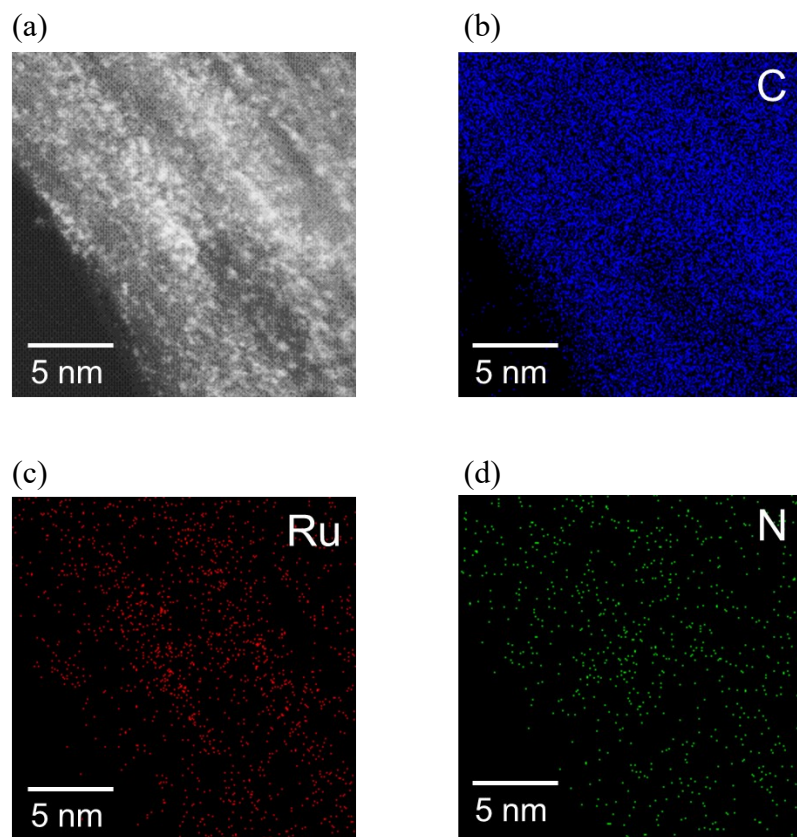


Fig. S3. (a) STEM image and elemental maps of  $\text{Li}^+$ -receptor/CNT: (b) C K, (c) Ru L, and (d) N K signal maps.

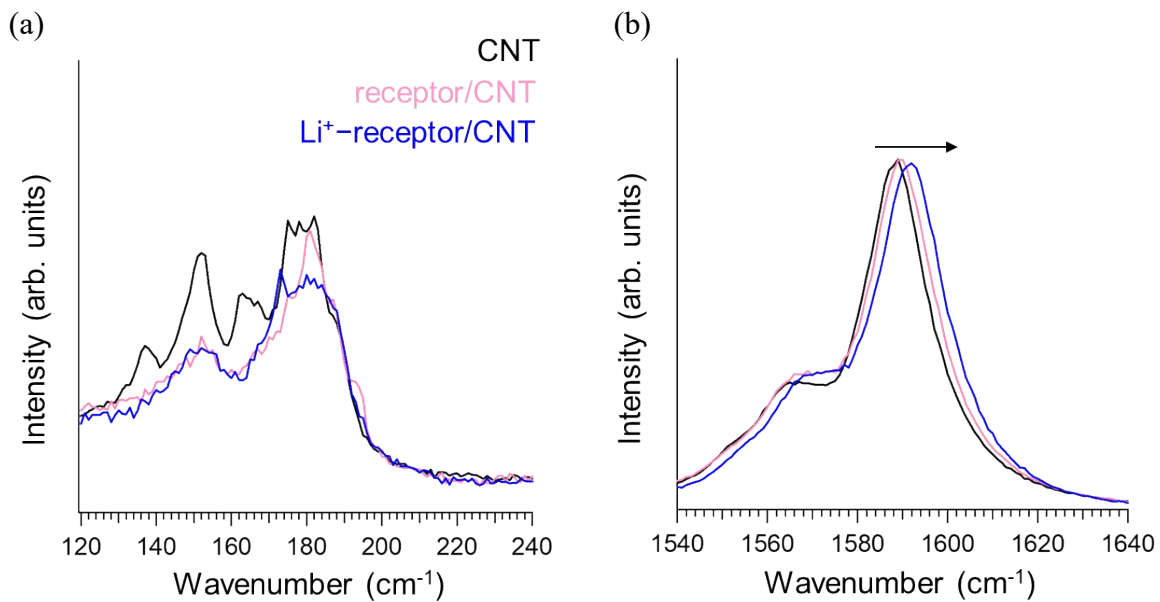


Fig. S4 Normalized Raman spectra (a) in the low-frequency radial breathing mode range and (b) at the G-band. Color code: CNT, black; receptor/CNT, pink;  $\text{Li}^+$ -receptor/CNT, blue.

To investigate the dehydration behavior of H<sub>2</sub>O on the sample, TGA was performed in an N<sub>2</sub> environment (Fig. S3). From 323 to 373 K, an apparent weight loss of 2.6 wt% can be observed in Receptor/CNT, which is attributed to the evaporation of adsorbed water and can probably be regarded as the desorption of physisorbed nonhydrated water. By contrast, the Li<sup>+</sup>-receptor/CNT exhibits a larger major weight loss after the water evaporation temperature of 373 K, which is considered the loss of hydrated water chemisorbed on the sample.<sup>4,5</sup> When the measured temperature reached 492 K, the weight loss was 6.1 wt%. Overall, this sample shows the presence of more adsorbed water than Receptor/CNT.

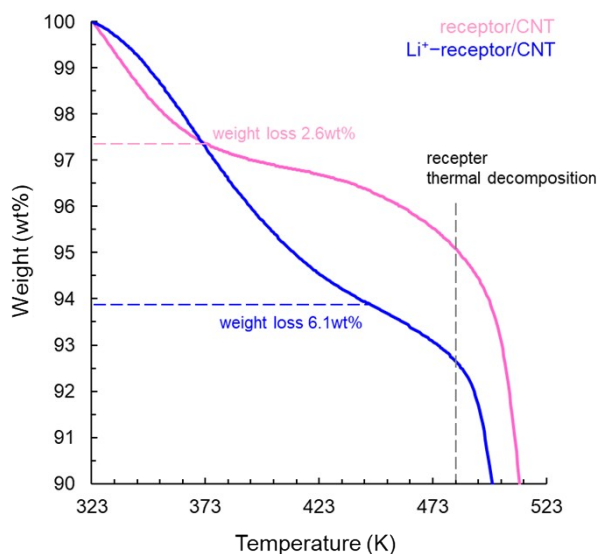


Fig. S5 Thermogravimetric analysis curves of CNT films prepared in various solvents in the presence of flowing N<sub>2</sub> at 150 mL min<sup>-1</sup> and measured at a heating rate of 10 K min<sup>-1</sup>.

## References

1. M. K. Patel, R. Fox and P. D. Taylor, *Tetrahedron*, 1996, **52**, 1835.
2. Z. Grote, M.-L. Lehaire, R. Scopelliti and K. Severin, *J. Am. Chem. Soc.*, 2003, **125**, 13638.
3. B. A. MacLeod, N. J. Stanton, I. E. Gould, D. Wesenberg, R. Ihly, Z. R. Owczarczyk, K. E. Hurst, C. S. Fewox, C. N. Folmar, K. H. Hughes, B. L. Zink, J. L. Blackburn and A. J. Ferguson, *Energy Environ. Sci.*, 2017, **10**, 2168.
4. S. Wang, X. Xu, C. Cui, C. Zeng, J. Liang, J. Fu, R. Zhang, T. Zhai and H. Li, *Adv. Funct. Mater.*, 2022, **32**, 2108805.
5. C. G. Tang, M. N. Syafiqah, Q.-M. Koh, M. C.-Y. Ang, K.-K. Choo, M.-M. Sun, M. Callsen, Y.-P. Feng, L.-L. Chua, R.-Q. Png and P. K. H. Ho, *Nat. Commun.*, 2023, **14**, 3978.