

Cu-ion-induced n- to p-type switching in organic thermoelectric polyazacycloalkane/carbon nanotubes

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Characterization

The in-plane thermoelectric properties of the thermoelectric conversion sheets were examined using a ULVAC ZEM-3 M8 instrument (ULVAC-RIKO Inc., Japan) in a He atmosphere at a reduced pressure (0.01 MPa). All the samples were preheated to 380 K (=107 °C) for 30 min and evaluated at least three times at 345 K (= 72 °C). The CNT-based films were examined through the field-emission scanning electron microscopy (FE-SEM) technique using an S-4800 Type 2 instrument (Hitachi, Japan). An ultraviolet–visible–near-infrared spectrophotometer (UH4150, Hitachi High Technologies, Co.) was used to identify the association state of copper complex formation in the aqueous solution. The standard

deviation of the average bundle diameter was calculated by measuring the diameters of 200 CNTs through enlarged SEM images. Transmission electron microscopy (TEM) images were recorded on JEOL JEM-1230 instrument at an accelerating voltage of 200 kV, and some representative micrographs are shown in Figure S2. For these observations, a 10-fold diluted drop-casting solution was used; the solution was sonicated for 10 min and dropped onto a Cu grid, where it dried spontaneously. Raman spectra were obtained using an NRS-7100 laser Raman spectrometer (JASCO, Japan) with a 532 nm green-line laser. N₂ adsorption isotherms were acquired at 77 K by a BELSORP MAX instrument (MicrotracBEL Corp.). Each sample was activated prior to the analysis by heating at 353 K for 12 h in a reduced pressure environment ($< 10^{-2}$ Pa). Because it is difficult to peel the CNT film from the polyimide sheet, a CNT-independent sheet prepared on a polytetrafluoroethylene chelate was used to obtain the gas-adsorption measurements. Sample films with thickness errors of ± 1.0 μm or less were prepared using the abovementioned method. For oxygen-resistance tests, cyclen/CNT films were cut into rectangular pieces (4 mm \times 16 mm), placed in glass Petri dishes, and incubated in air at room temperature (298 K and 60% RH). The samples were thermoelectrically examined at 345 K periodically over the course of 14 days, and the results are shown in Figure S6.

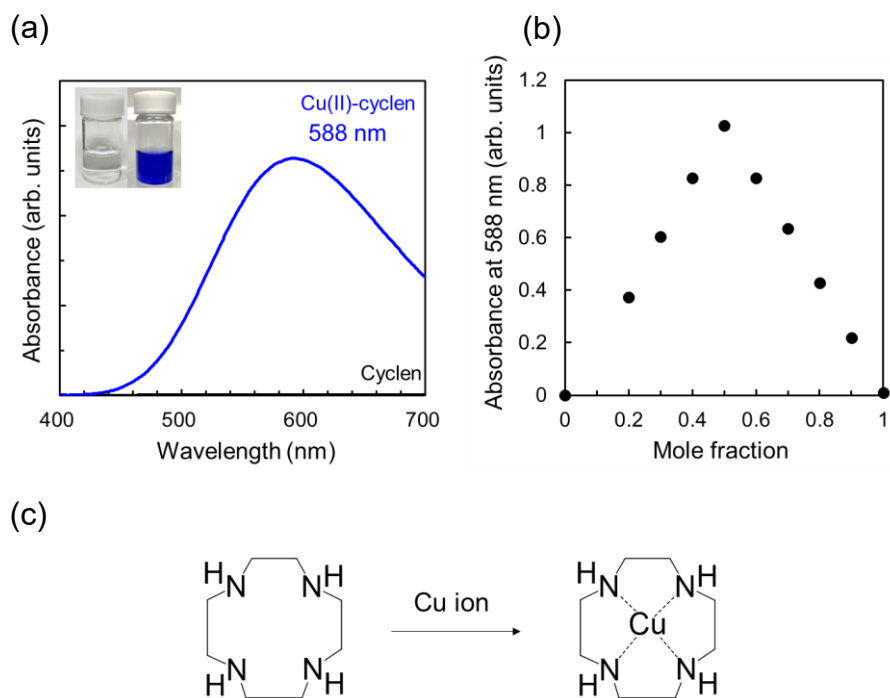
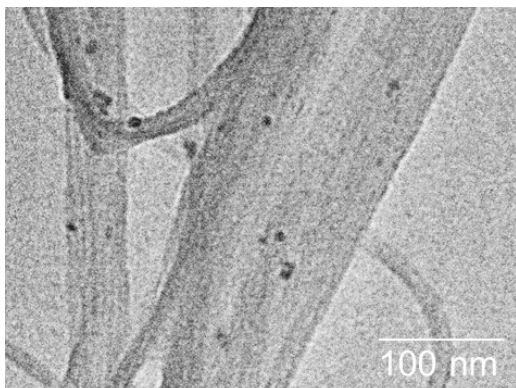
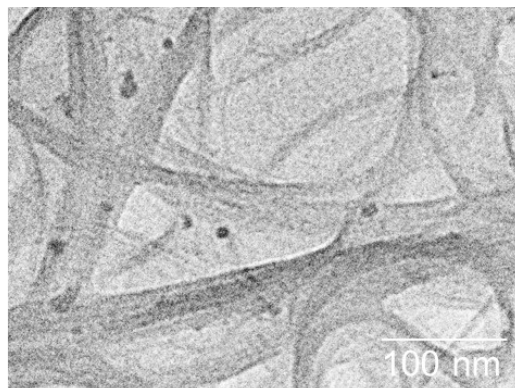


Figure S1. (a) UV/Vis spectra of the aqueous solution of cyclen and Cu ion before (black) and after (blue) the reaction solution. The photograph shows the color change from the beginning to the end of the conversion. (b) Job's plot analysis for the complexation of cyclen with Cu ion. The total concentration of cyclen + copper ion was maintained constant at 16.7 mM. (c) Preparation scheme of metal-complexes consisting of cyclen and Cu ions.

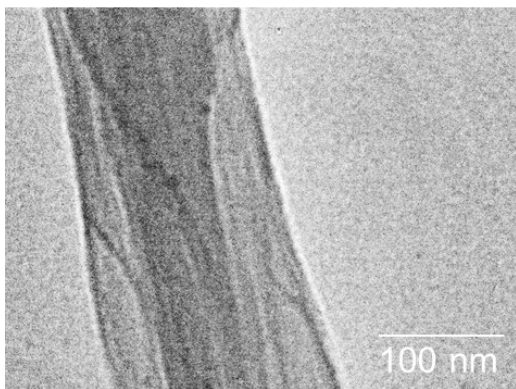
(a)



(b)



(c)



(d)

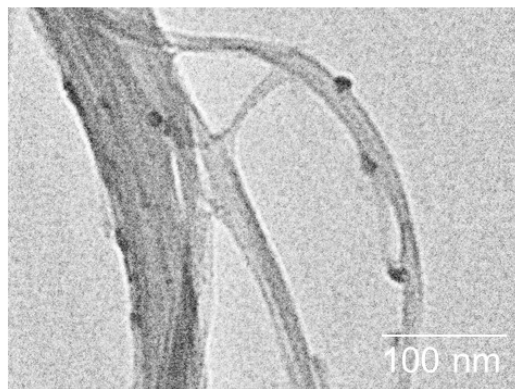


Figure S2. TEM images of (a, b) cyclen/CNT and (c, d) Cu(II)-cyclen/CNT.

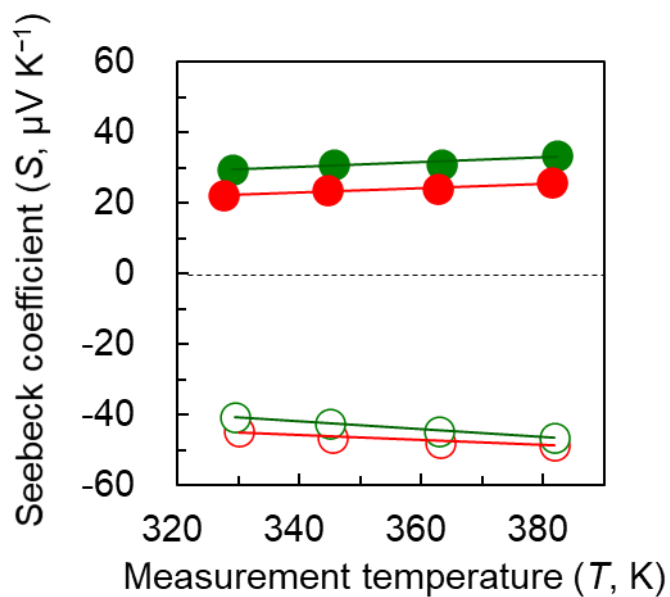


Figure S3. Seebeck coefficient of cyclam/CNT (red) and TACN/CNT (green) as functions of temperature. The closed circles indicate the state after Cu ion addition.

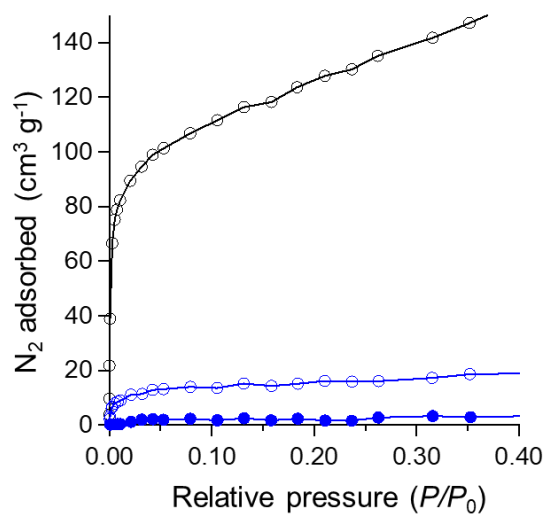


Figure S4. N₂ adsorption isotherms at 77 K: narrow range; color code: CNT, black; cyclen/CNT, blue (open circles); Cu(II)-cyclen/CNT, blue (closed circles).

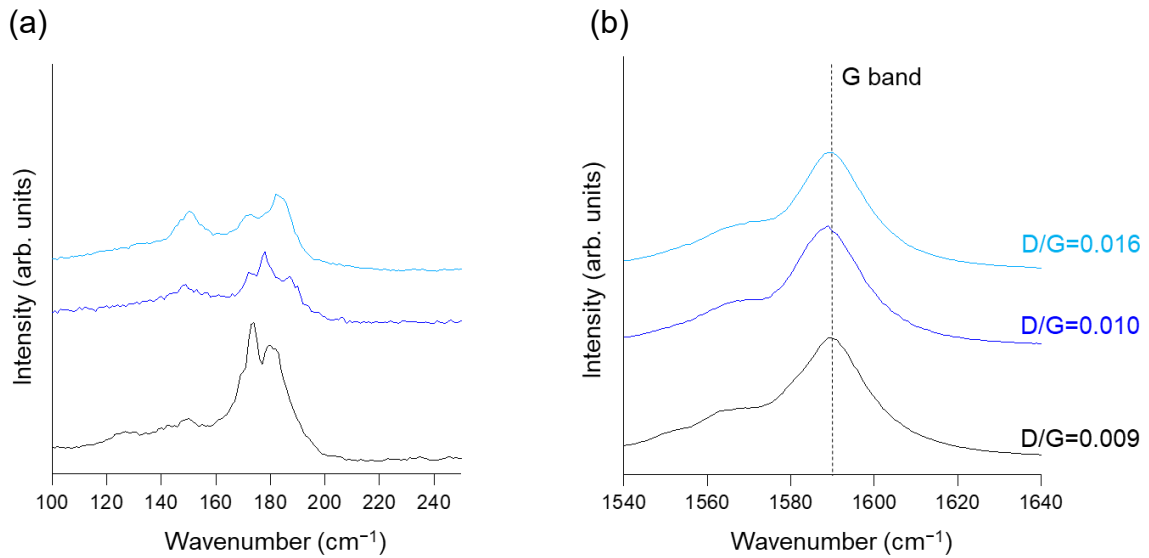


Figure S5. Normalized Raman spectra (a) in the low-frequency radial breathing mode range and (b) at the G-band. Color code: CNT, black; cyclen/CNT, blue; Cu(II)-cyclen/CNT, light blue.

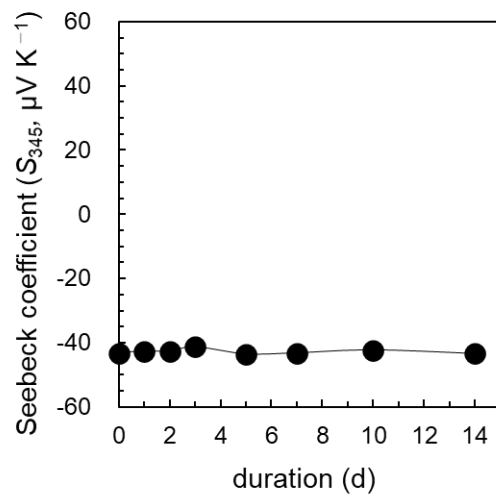


Figure S6. Temporal changes in the Seebeck coefficient of cyclen/CNT at 298 K in an ambient atmosphere. Measurements were performed at 345 K in He.

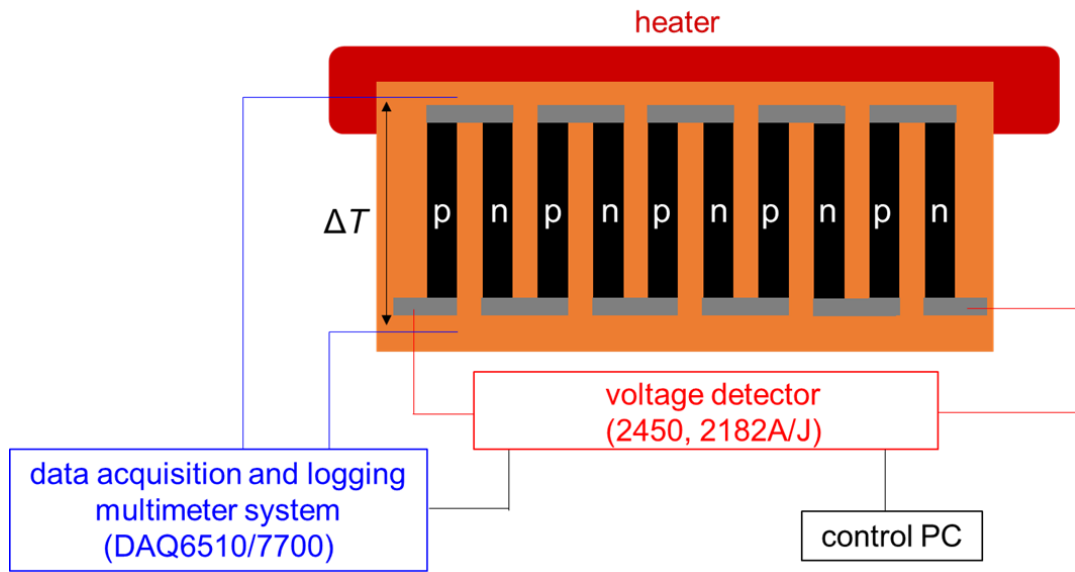


Figure S7. Schematic of the fabricated thermoelectric power conversion device.

Table S1. Performance of Thermoelectric modules in previous studies and that prepared in this study. Details of the module structure (sample, carrier type, preparation solvent, p–n leg number, temperature difference, power, and year of publication) are provided. Carbon nanotube is abbreviated as CNT.

Sample	Carrier type	Preparation solvent /Post-processing	p–n legs	ΔT (K)	Power (μW)	Year	Reference
Cu(II)-cyclen/CNT cyclen/CNT	p n	water water	5	75	1.36	–	This work
CNT pyridineborane/CNT	p n	– ethanol aqueous solution	5	66	1.15	2021	58
benzothienobenzothiophene-charge transfer complex/CNT benzothienobenzothiophene-charge transfer complex/CNT	p n	chlorobenzene triethylamine	5	38	0.34	2021	59
naphthalene diimide derivatives/CNT naphthalene diimide derivatives/CNT	p n	chlorobenzene triethylamine	5	65	2.81	2020	60
CNT polyethylenimine/CNT	p n	ethanol/N ₂ annealed water	8	49.5	1.16	2020	61
CNT acridine derivatives/CNT	p n	– dimethyl sulfoxide	5	74.8	1.88	2019	43
CNT cetyltrimethylammonium bromide/CNT	p n	ethanol N,N-dimethylformamide	5	80	6.7	2018	62
poly(3,4-ethylenedioxythiophene) polystyrene sulfonate/CNT fullerene/TiS ₂ hybrid	p n	water isopropyl alcohol	2	20	0.335	2018	63
poly(3,4-ethylenedioxythiophene) polystyrene sulfonate TiS ₂ hybrid	p n	ethylene glycol aqueous solution N-methylformamide	5	70	0.90	2017	64
CNT diethylenetriamine-CaH ₂ /CNT	p n	ethanol aqueous solution ethanol aqueous solution	14	55	0.65	2016	65
negative charged polyelectrolytes/CNT positive charged polyelectrolytes/CNT	p n	methanol aqueous solution methanol aqueous solution	4	35	0.30	2015	66