Electronic Supplementary Information (ESI) for

Crown ether salt-doped ladder-type conducting polymers for air-stable n-type thermoelectric materials

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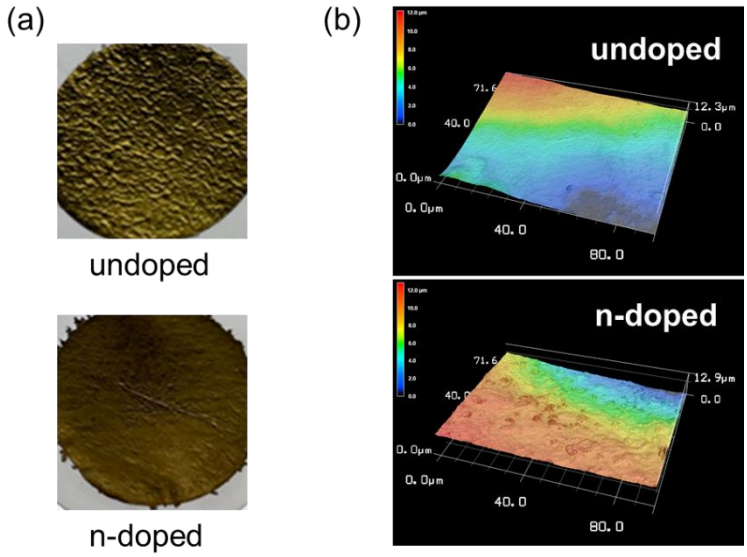

Figure S1. Surface morphology. (a) Digital photographs and (b) laser microscopy images of undoped and n-doped BBL films. Scale unit for (b) is μm.

In order to ensure the reliability of thermoelectricity measurements with Advance Riko Inc. ZEM-3, we confirmed that the resistivity of every samples is below 10 kohm. In this case, the sample thickness was optimized above 15 micrometers. The thickness and roughness were evaluated using thickness gauge and laser microscopy.

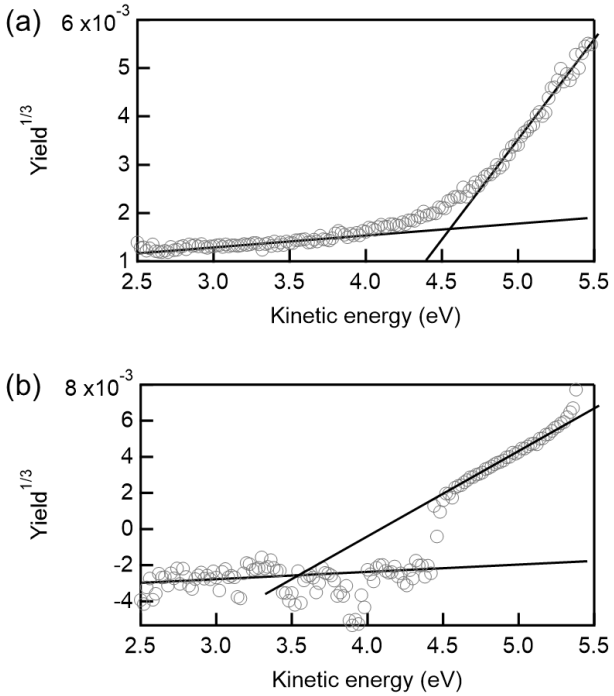

Figure S2. Doping level analysis. Ultraviolet photoelectron yield spectroscopy of (a) pristine and (b) n-doped BBL films in vacuo.

We have tried to more quantitatively evaluate the doping level of BBL films using several methods, in addition to electrical conductivity. The straightforward ways include photoelectron spectroscopy; although the photoelectron signal was too weak to discuss, ultraviolet photoelectron yield spectroscopy (UPYS) in the laboratory (Riken Keiki) was likely to show higher energy shift, suggesting n-type doping.

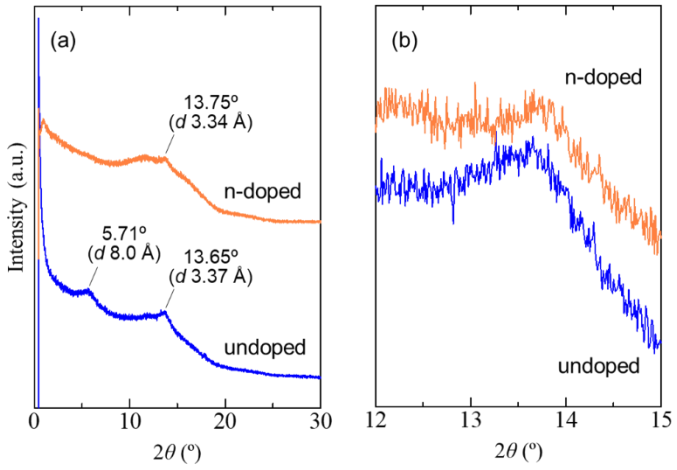

Figure S3. Crystallinity evaluation. Powder X-ray diffraction (PXRD) patterns of undoped and n-doped BBL obtained at SPring-8 BL44B2[S1,S2] (λ = 0.8 Å). (b) is a magnification of (a) featuring the π-stacking distance. A slight shift of the diffraction at 2θ = 13.65° (*d*-spacing = 3.37 Å) to 13.75° (*d*-spacing = 3.34 Å) suggests a stronger π-π stacking interaction after n-doping, while a disappearance of the diffraction at 5.71° (*d*-spacing = 8.0 Å) shows the destruction of lamellar stacking.[S3]

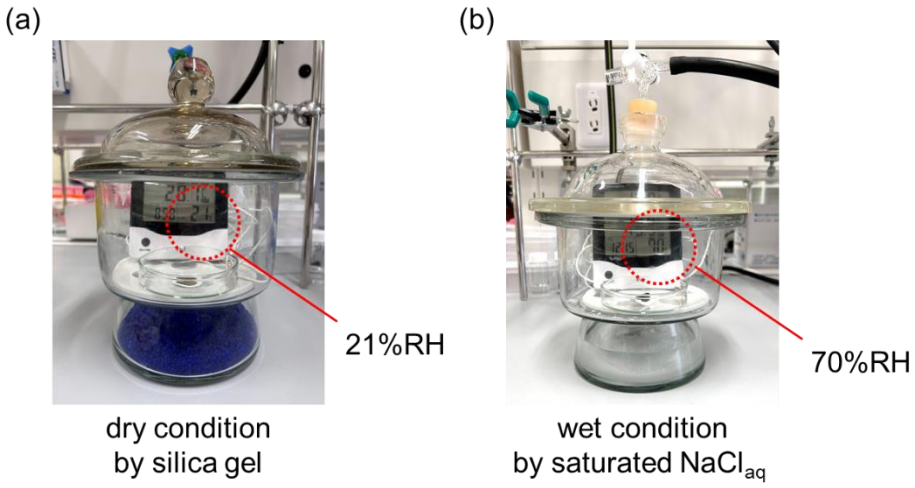

Figure S4. Environmental tests. Digital photographs of (a) a dry chamber with silica gel and (b) a wet chamber with saturated NaCl aqueous solution. The latter was fully filled with nitrogen gas.

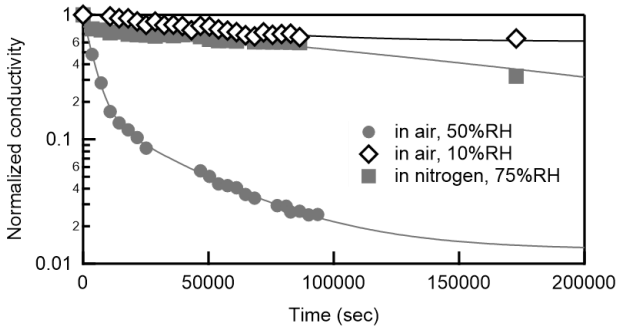

Figure S5. Conductivity decay dependences on environments for N-DMBI-doped BBL films.

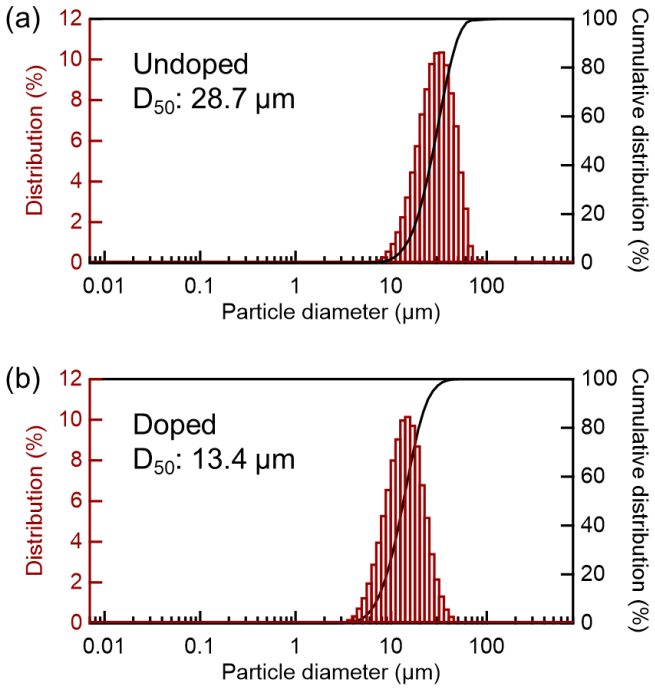

Figure S6. Particle size distribution of BBL particles (a) before and (b) after n-doping estimated using the laser diffraction (Shimadzu SALD-7500nano).

Materials and methods

Film preparation. Polybenzimidazobenzophenanthroline (BBL, Sigma-Aldrich) was used as purchased. BBL colloidal suspension was prepared by the modified Fabiano's method. Typically, 3.0 mg BBL was dissolved in 1.5 mL methanesulfonic acid (MSA, ≧99.0%, Nacalai Tesque), followed by precipitation with excess (approximately 6.0 mL) ethanol (FUJIFILM Wako Chemicals). The precipitates were washed using methanol six times, and were then mixed with N,N-dimetylformamide (super-dried for organic synthesis, ≧99.5%, FUJIFILM Wako Chemicals) containing the fixed amounts of n-dopants, in a nitrogen-filled three-necked flask. The representative n-doping was performed using the mixture of 18-crown-6-ether (≧98.0%, Nacalai Tesque) and potassium hydroxide (Guaranteed Reagent, FUJIFILM Wako Chemicals), as well as 4-(1,3-Dimethyl-2,3-dihydro-1H-benzimidazol-2-yl)-N,N-dimethylaniline (N-DMBI, ≧ 95.0%, Tokyo Chemical Industry). The mixture was heated at 80–120 ºC, for 1 hours, followed by vacuum filtration with membrane filters (0.22 m pore size, hydrophilic PTFE membrane, 25 mm diameter, Merck Millipore). The films were dried in vacuo at 160 ºC, and then subject to further experiments.

Methods. Optical absorbance was evaluated using a spectrophotometer (Shimadzu UV-3600Plus). Electrical conductivity and the Seebeck coefficient were measured using a

commercial thermoelectric properties measurement system (Advance Riko ZEM-3). Time-course electrical conductivity was tracked using Nittoseiko Analytech Roresta-GX MCP-T700. Ultraviolet photoelectron yield spectroscopy was conducted using Bunkoukeiki BIP-KV100. Particle size analysis was performed by Shimadzu SALD-7500nano. Powder X-ray diffraction (PXRD) patterns were obtained at SPring-8 BL44B2S1,S2 (λ = 0.8 Å).

Doping level analysis

Ultraviolet photoelectron yield spectroscopy revealed the work function shift of 0.5–1.0 eV, before and after treatment with KOH/18-crown ether, supporting the successful n-doping. This fact is consistent with UV-Vis absorption results. It should be noted that the profiles of the both UV-Vis spectroscopy and UPS even after n-doping involve the features of undoped BBL. Absorption spectra showed the 660 nm peak derived from neutral BBL and UPS exhibited a significant rise in the 4.5-5.0 eV range. We believe that this doping inhomogeneity results from accessibility of dopants to the core of BBL particles. BBL colloids possess significant particle sizes (Figure S6), where BBL molecules in the core might rarely be doped.

Accuracy of thermoelectric properties

Due to measurement limitation, the electrical conductivity and Seebeck coefficient presented here contain 10% and 15% errors, respectively. In order to improve statistical reliability, we have measured the thermoelectric properties of three different samples at eight doping conditions (totally 24 plots) in Figure 4b.

References

S1 K. Kato and H. Tanaka, *Adv. Phys. X*, 2016, **1**, 55–80.

S2 K. Kato, Y. Tanaka, M. Yamauchi, K. Ohara and T. Hatsui, *J. Synchrotron Radiat.*, 2019, **26**, 762–773.

S3 C.-Y. Yang, M.-A. Stoeckel, T.-P. Ruoko, H.-Y. Wu, X. Liu, N. B. Kolhe, Z. Wu, Y. Puttisong, C. Musumeci, M. Massetti, H. Sun, K. Xu, D. Tu, W. M. Chen, H. Y. Woo, M. Fahlman, S. A. Jenekhe, M. Berggren and S. Fabiano, *Nat. Commun.*, 2021, **12**, 2354.