Electronic Supplementary Information

# Enhancing thermal stability of n-type conduction in carbon nanotubes via cation replacement mediated by bicyclic guanidinium salts

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**Table S1.** List of chemicals and materials used in this study.

| | purity (%) | supplier | remark |
|---|---|---|---|
| Carbon nanotube | 99 | OCSiAl | Single-walled CNT. Tuball. Diameter: 1.6±0.4 nm. |
| Brij L4 | 80 | Sigma | Nonionic surfactant |
| Acetone | >99.0 | Nacalai | |
| Acetonitrile | 99.5 | Nacalai | |
| TBD | ≥98.0 | TCI[†] | |
| HCl | – | FUJIFILM[‡] | 35.0–37.0 wt% aqueous solution |
| $HNO_3$ | – | Nacalai | 60–61 wt% aqueous solution |
| Li-TFSI | >98.0 | TCI | |
| $CoCp^*_2$ | – | Sigma | |

[†]TCI: Tokyo Chemical Industry; [‡]FUJIFILM: FUJIFILM Wako Pure Chemical

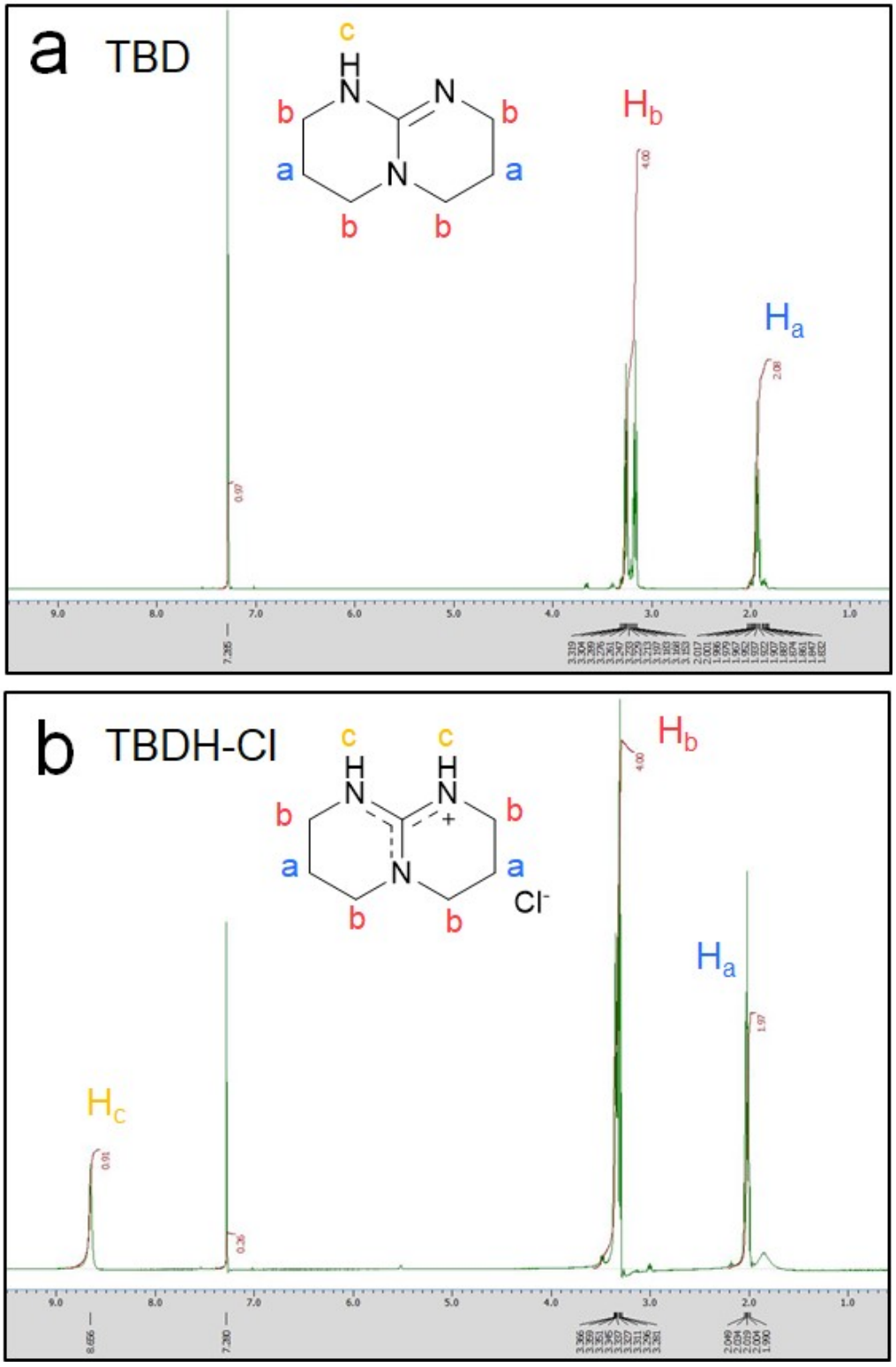


**Fig. S1.** $^{1}$H NMR spectra of (a) TBD (as comparison) and (b) synthesized TBDH-Cl. Spectra of TBDH-$NO_3$ and TBDH-TFSI can be found in our previous study.[S1]

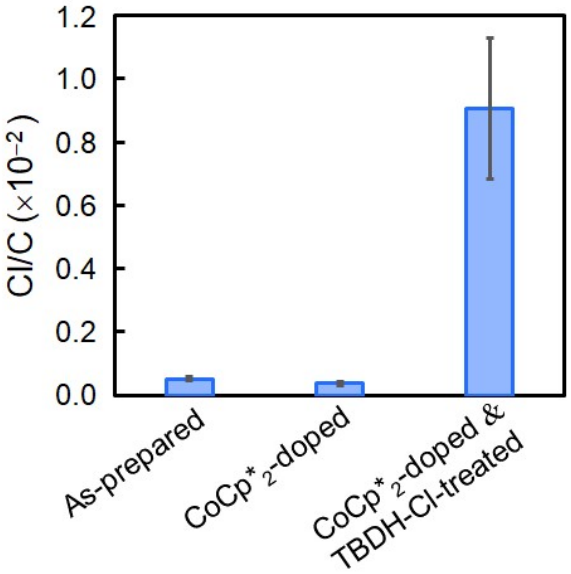


**Fig. S2.** Compositional ratios of chlorine to carbon (Cl/C) in as-prepared, $CoCp^*_2$-doped, and $CoCp^*_2$-doped followed by TBDH-Cl treatment of CNT films, derived from the data in Figure 5a of the main article. Data statistics: $n$ = 3; error bars represent standard deviations (SDs).

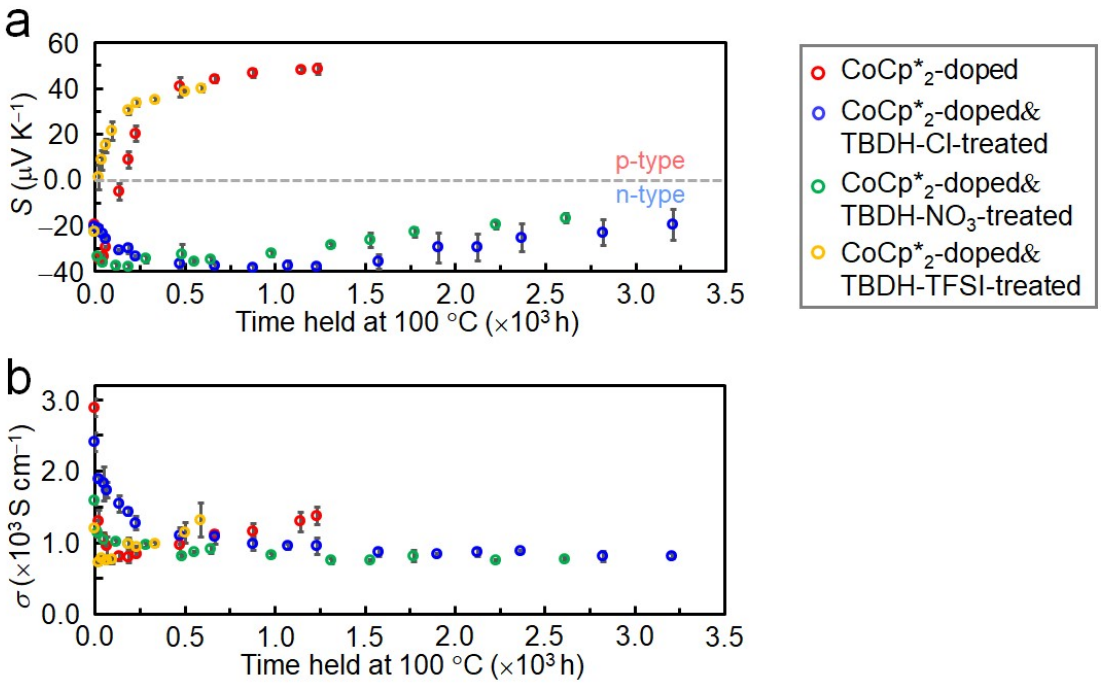


**Fig. S3.** Variation with time in (a) Seebeck coefficient ($S$) and (b) electrical conductivity ($\sigma$) of $CoCp^*_2$-doped and TBDH-X- ($X^- = Cl^-$, $NO_3^-$ or $TFSI^-$) treated CNT films during incubation at 100 °C in air. Data statistics: $n$ = 3; error bars represent SDs.

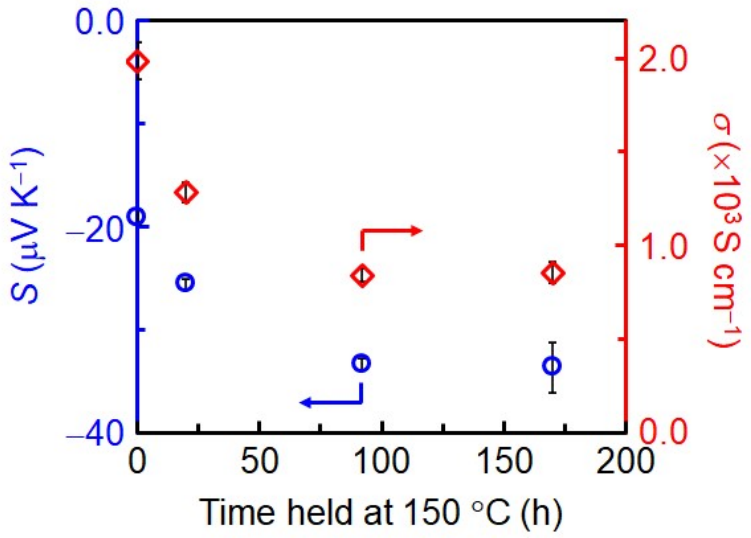


**Fig. S4.** Variation with time in Seebeck coefficient ($S$) and electrical conductivity ($\sigma$) of TBD-doped CNT films during incubation at 150 °C in air. Data statistics: $n = 3$; error bars represent SDs. Considering the faster depletion behaviors in these parameters than those during incubation at 100 °C in air reported in our previous papers,[S1,S2,S3] the retention ability of n-doped states of CNTs becomes poor at the higher temperatures. On the other hand, our previous study revealed that the TBD-doped CNTs showed decrease in electrical conductivity while retaining the negative Seebeck coefficient in high-humid conditions.[S3] The once decreased conductivity recovered by evacuating. The adsorbed water molecules seemed to contribute to the decrease of electron mobility rather than dedoping. Based on these considerations, we set the incubation temperature as 100 °C throughout the study to confirm the effect of cation replacement on the stability of n-doped states.

**Table S1** Comparison of power factors of n-type materials. Note that the power factor is a metric for comparing power output of materials; dimensionless figure of merit (including thermal conductivity) is important to comparatively evaluate the heat-to-electricity energy conversion efficiency.

| Material | Power factor ($\mu W\ m^{-1}\ K^{-2}$) | Ref. |
|---|---|---|
| CNT | 150 | 25 |
| CNT | 100–150 | 26 |
| CNT | 82–86 | 27 |
| CNT | 230 | 28 |
| CNT | 261 | 34 |
| CNT | 258 | 50 |
| poly(benzodifurandione) | 90 | 48 |
| CNT | 62–101 | This study |

## Reference


(S1) M. Nishinaka, I. Harada, K. Akaike, Q. Wei, Y. Koshiba, S. Horike, K. Ishida, Electrochemical charge-carrier modulation of carbon nanotubes using ionic liquids derived from organic superbases for stable thermoelectric materials, *Carbon*, 2024, **218**, 118667.

(S2) S. Horike, Q. Wei, K. Akaike, K. Kirihara, M. Mukaida, Y. Koshiba and K. Ishida, *Nat. Commun.*, 2022, **13**, 3517.

(S3) M. Nishinaka, Q. Wei, Y. Koshiba and S. Horike, *Energy Mater. Adv.*, 2024, **5**, 0123.