Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
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Electronic Supplementary Information (ESI):

Nonoguchi et al. "Electrochemical n-type doping of carbon nanotube films by supramolecular electrolytes"

Air-stability

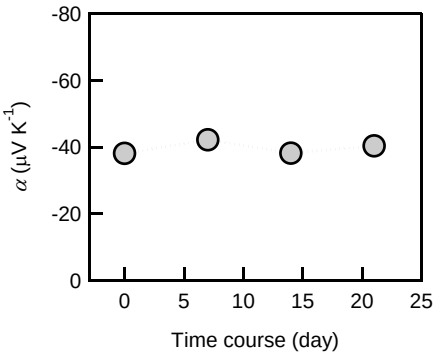

Figure S1. Time course test of the thermoelectric properties of n-type SWNT films electrochemically-doped under -1 V bias.

Doping progress monitoring

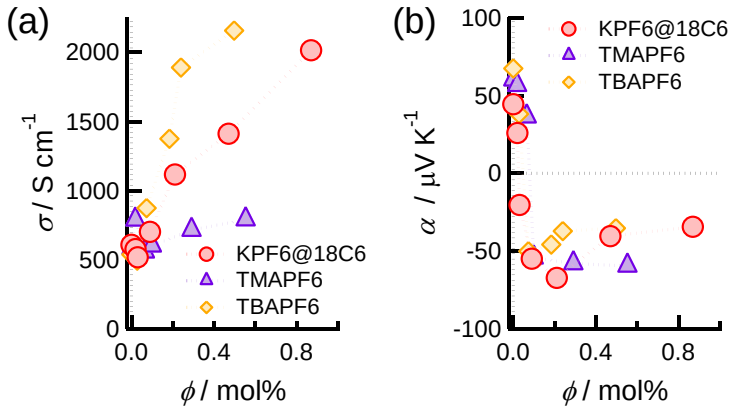

Figure S2. Thermoelectric properties dependent on electrolytes. (a) Electrical conductivity and (b) the Seebeck coefficient of SWNT electrodes.

SWNT electrode morphology

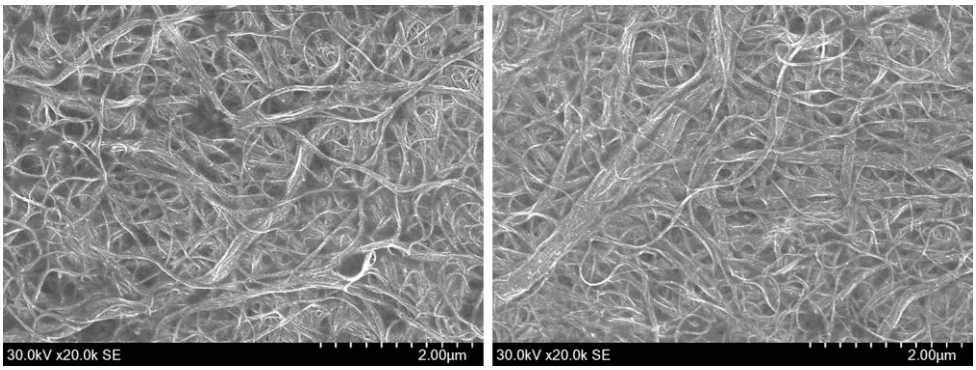

Figure S3. SEM images of electrochemically-doped SWNT electrodes. Mesoporous structures allow the electrolyte to penetrate the whole electrode, which could enable uniform doping.

Synthesis of benzo-21-crown-7

Benzo-21-crown-7-ether was synthesized according to literature procedures [ref. S1]. A mixture of catechol (1.15 g, 10.46 mmol), K_2CO_3 (4.34 g, 3 eq), KPF_6 (2.89 g, 1.5 eq) and hexa(ethylene glycol) ditosylate (6.18 g, 1 eq) in 80 mL CH_3CN was stirred and refluxed for 48 hours under nitrogen gas protection. After cooling, the mixture was filtered and CH_3CN was removed with a rotaevaporator, and then 150 mL CH_2Cl_2 was added. After washing with water several times, the organic phase was dried with Na_2SO_4 and then concentrated. The residue was purified by almina column chromatography (hexane/ethyl acetate, v/v 1:1) to provide benzo-21-crown-7 (2.42 g, 65%). The proton NMR spectrum of the pure benzo-21-crown-7 is shown below. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ (ppm): 6.88–6.93 (4H, m), 4.15–4.19 (4H, t), 3.93–3.94 (4H, t), 3.79 (4H, m), 3.75 (4H, m), 3.66–3.68 (8H, m).

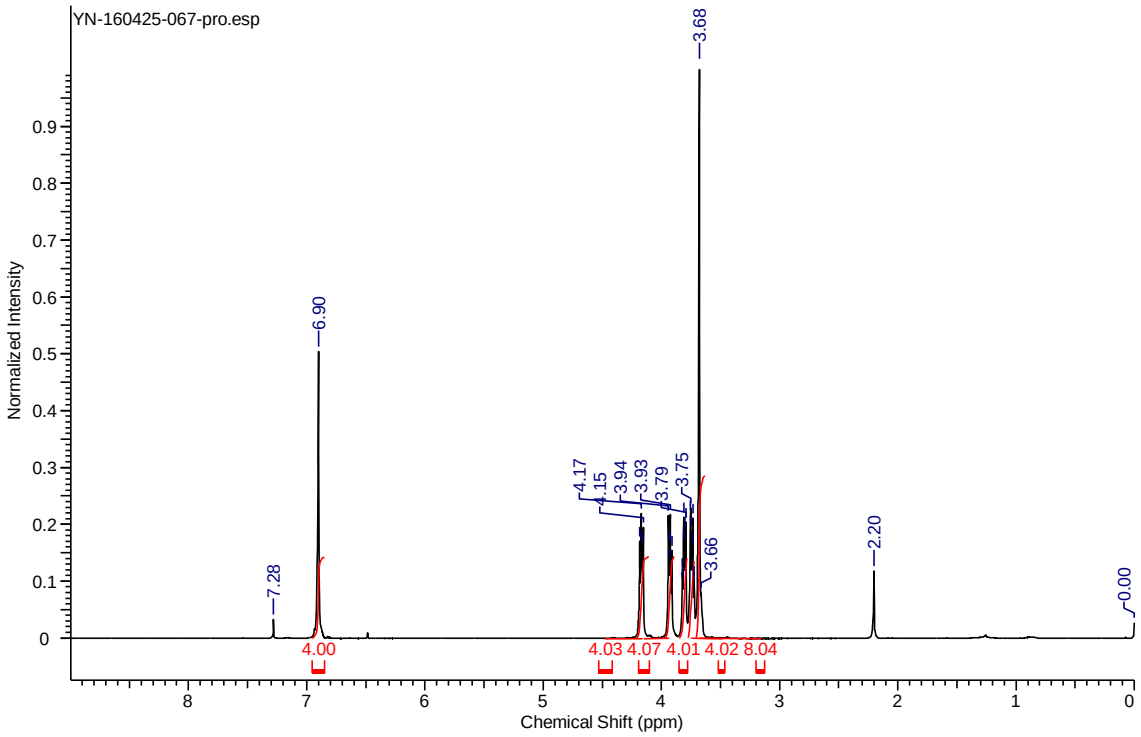

Figure S4. NMR spectrum of benzo-21-crown-7-ether.

Electrochemistry

We use a standard electrochemistry configuration with a Pt counter electrode, a non-aqueous Ag/AgCl reference electrode, and a potentiostat (Hokuto Denko HSV-110). SWNT films are used as working electrodes (Figure S3).

Materials

For spectroelectrochemistry, SWNTs (Meijo Nanocarbon EC-2.0) were first dispersed in 1% Pluronic F127 aqueous solution by tip-sonication for 20 minutes. Its supernatant after centrifugation at 10000 rpm for 1 hour was filtered on a 0.2 μm-pore PTFE membrane. The dried membrane-supported SWNT thin film was mechanically transferred to a 0.1mm-thick PET film, prior to the electrochemical doping. Nanotube film thickness was controlled

between 400-600 nm. A controlled potential was then applied to SWNT films for sixty seconds in acetonitrile solution containing 0.1 M electrolytes. The films were taken out from the electrolyte solution, and were well dried before absorption measurements. Thick films were prepared by the reported procedure [ref. S2].

Physical characterization

Electrical conductivity and the Seebeck coefficient are measured by standard four-probe and two-probe methods (Mitsubishi Chemical MCP-T610, and MMR Technologies K20SB100-3R), respectively. The Seebeck coefficient data contain approximately 15 % errors.

References:

[S1] C. J. Zhang, S. J. Li, J. Q. Zhang, K. L. Zhu, N. Li, F. H. Huang, *Org. Lett.* **2007**, *9*, 5553-5556.

[S2] a) Y. Nonoguchi, K. Ohashi, R. Kanazawa, K. Ashiba, T. Nakagawa, C. Adachi, K. Hata, T. Tanase, T. Kawai, *Sci. Rep.* **2013**, *3*, 3344; b) Y. Nonoguchi, Y. Iihara, K. Ohashi, T. Murayama, T. Kawai, *Chem. Asian J.* **2016**, *11*, 2423-2427; c) Y. Nonoguchi, S. Sudo, A. Tani, T. Murayama, Y. Nishiyama, R. M. Uda, T. Kawai, *Chem. Commun.* **2017**, *53*, 10259-10262.