



Electrochemical n-type doping of carbon nanotube films by supramolecular electrolytes

| | |
|-------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Journal: | <i>Journal of Materials Chemistry A</i> |
| Manuscript ID | TA-COM-04-2018-003948.R1 |
| Article Type: | Communication |
| Date Submitted by the Author: | 26-May-2018 |
| Complete List of Authors: | Nonoguchi, Yoshiyuki; Nara Institute of Science and Technology, Division of Materials Science Kojiyama, Keita; Nara Institute of Science and Technology, Division of Materials Science KAWAI, TSUYOSHI; Nara Institute of Science and Technology, Division of Materials Science |
| | |



Journal Name

COMMUNICATION

Electrochemical n-type doping of carbon nanotube films by supramolecular electrolytes

Yoshiyuki Nonoguchi,^{*a,b} Keita Kojiyama^a and Tsuyoshi Kawai^{*a}Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

In this paper, we demonstrate the electrochemical n-type doping of single-walled carbon nanotubes with supramolecular electrolytes. Quantitative electrochemical charging allows the tunable conversion of p-type SWNT films to their n-type forms. Its conversion and stability of the products are found to rely on supramolecular cation structures.

The chemical doping of π -electron systems has been studied as a crucial procedure for tuning carrier transport in organic thermoelectric materials.¹⁻³ The doping can modulate the polarity between p- and n-type materials, and adjust their carrier concentration and the Fermi level associated with redox states.^{4,5} As most π -conjugated organic and carbon-based materials preferentially convey positive charges, oxidizing reagents such as F4TCNQ are adopted to tune the oxidation state in the p-type materials. Systematically controlled doping has elucidated the unique relationship between conductivity and thermopower in organic semiconductors,⁶ however, the reliable and precisely controlled n-type doping of carbon-based thermoelectric materials, remains a challenge. This is partly because of the instability of n-doped π -electron systems in carbon-based materials and difficulty in the evaluation of doping levels. Improvements in both the thermoelectric performance of organic semiconductors with high stability and the design of stable dopants remain under investigation.⁷⁻¹¹

Due to their low-lying conduction band levels, single-walled carbon nanotubes (SWNTs) are expected to enable the investigation of chemical n-type doping.¹² The n-doping of SWNTs has long been examined using electron donors. For example, polyethylene imine (PEI) is well recognized for n-type doping, but its stability is limited by oxygen adsorption and its oxidation.^{13,14} Furthermore, it is empirically recognized that

most reported n-type SWNTs substantially degrade in air and this degradation remains unsettled. From an electrochemical point of view, electrons are injected into SWNTs in n-type doping. Electron-rich carbons generated by n-doping are likely to behave as nucleophiles, and react with electrophiles such as oxygen and water.¹⁵ In order to reduce their reactivity in the n-doped state, we have recently proposed that delocalized negative charges in n-type SWNTs could be stabilized using metal-crown ether complexes with delocalized positive charges (Scheme 1 (a)).¹⁶ This concept is an analogue to the Pearson's hard/soft acids/bases (HSAB) rule.¹⁷ This supramolecular approach achieved unprecedented air stability in n-type SWNTs above 100 °C, and has been applied to develop high-performance thermoelectric sheets.¹⁸ Electron injection was also realized by anion-induced electron transfer via the naked anion effect.^{19,20}

The present challenges for the doping of SWNTs involve the quantitative evaluation of counter-ion effects on the reactivity and the stability of SWNT-counter ion complexes.^{10,11,21,22} Complexity in the chemical doping processes has concealed the intrinsic electron transfer chemistry underlying the n-type doping. In order to quantify the progress of doping and stability, here we propose the employment of electrochemical n-type doping with supramolecular crown ether complexes as electrolytes (Scheme 2).²³ First, we confirmed that the complexes of potassium hexafluorophosphate (KPF_6) and 18-crown-6-ether (**18C6**) serve as electrolytes. It is well recognized that these chemicals form an inclusion complex at sufficiently high complex formation constants in alcohol ($>10^3 \text{ M}^{-1}$), which is denoted as $\text{KPF}_6@18\text{C6}$. In this study, the PF_6^- anion (PF_6^-) was chosen since it is chemically inert. A standard electrochemistry configuration was used for charging a SWNT electrode with supramolecular electrolytes (Figure 1a). A potential was successfully applied using a SWNT sheet as a working electrode in the acetonitrile solution dissolving the complex electrolytes (the inset of Figure 1b). Chronoamperometry was then examined to count the Coulombic charges passing through the SWNT sheet (Figure 1b).

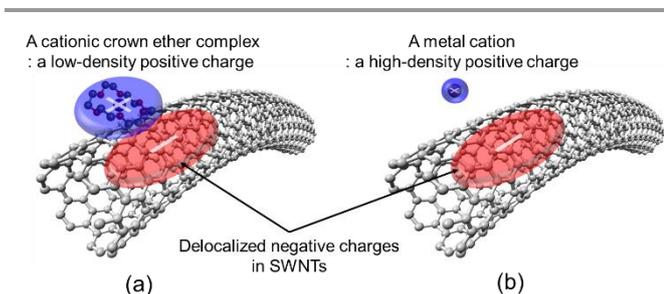
^a Division of Materials Science, Nara Institute of Science and Technology, Ikoma 630-0192, Japan. E-mail: nonoguchi@ms.naist.jp (YN), tkawai@ms.naist.jp (TK).

^b JST, PRESTO, Kawaguchi 332-0012, Japan.

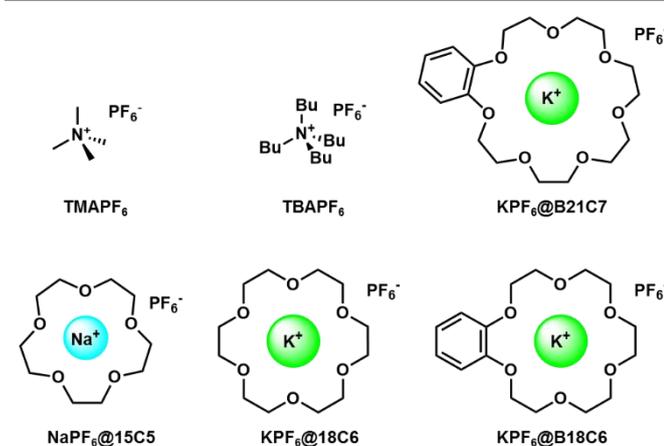
Electronic Supplementary Information (ESI) available: Experimental section, the synthesis of benzo-21-crown-7, characterization, and additional electrochemical doping data. See DOI: 10.1039/x0xx00000x

COMMUNICATION

During the chronoamperometry, most electrochemical charges are consumed for the reduction of SWNTs, forming the n-doped SWNTs; herein, denoted as a polaronic radical anion (SWNT^{-•}).



Scheme 1. Interaction of negatively charged SWNTs with counter cations. (a) Large-large, and (b) small-large cation-anion pairs.



Scheme 2. Supramolecular electrolytes in this work.

In order to confirm the n-type doping, absorption spectroscopy with dried SWNT thin films was conducted in the near-IR range. We fabricated for this purpose the conductive semi-transparent thin films of SWNTs on PET substrates.^{22c} After subtracting the background signal, we obtained the absorption spectrum of pristine SWNTs showing characteristic S₁₁ and S₂₂ bands at 0.44 eV and 0.78 eV, respectively (Figure 1c, 0V). The first S₁₁ transition is derived from the interband transition between the first van Hove singularity points. We observed characteristic suppression in this first band, dependent on applied bias (Figure 1c). The application of a -0.25 V bias led to the recovery of the S₁₁, as plotted in Figure 1d, indicating the neutralization of as-produced p-type SWNTs. Then, the S₁₁ band gradually decreased upon bias application below -0.5 V. A broad IR band below 0.3 eV was attributed to the one-dimensional plasmon resonance,²⁴ and was reversely decreased at -0.25 V, and increased below -0.5 V. These results suggest band filling in the early stage and carrier doping below -0.5V due to electrochemical n-type doping. Importantly, such spectral modulation was achieved due to the high stability of n-type species in air.

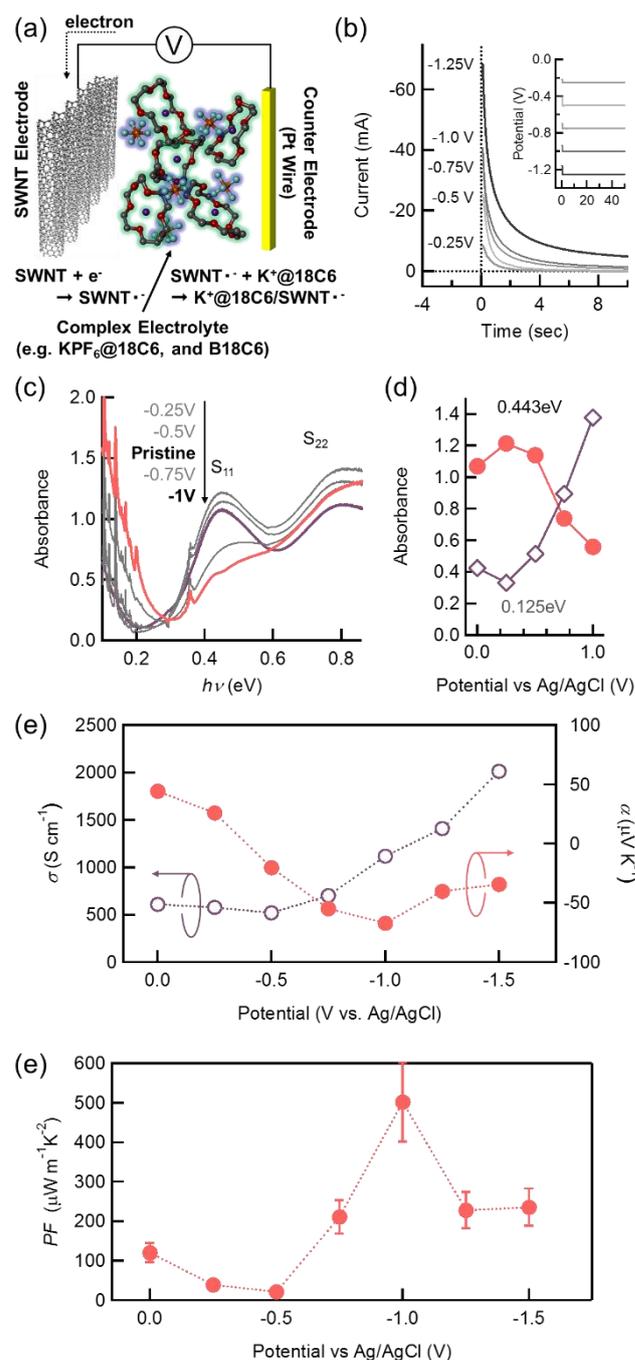


Figure 1. Supramolecular electrochemical doping. a) A schematic configuration of an experimental setup. b) Chronoamperometry profile of a SWNT electrode with a KPF₆@18C6 electrolyte. Inset shows potentials during the chronoamperometry. c) Temporal absorption change at each applied potentials. d) Conductivity (□), Seebeck coefficient (○), and e) power factor (PF) of SWNT films as a function of applied potentials for sixty seconds.

With this air stability of the n-doped state in mind, we studied the thermoelectric properties of electrochemically-doped, thick SWNT films. The electrical properties of SWNT films were measured after the electrochemical doping and drying process. Electrical conductivity (σ) slightly decreased at shallow negative potential and dramatically increased below -0.5 eV (Figure 1e). Additionally, the Seebeck coefficient (α) gradually dropped and its sign changed from positive to negative. These trends clearly indicate successful conversion to

an n-type form. Below the applied potential of -1.0 V, electrical conductivity dramatically increased and exceeded 1000 S cm^{-1} . At the same time, the Seebeck coefficient gradually decreased. These trade-off relationships can be clearly explained by the doping to the deep level.²⁵ This characterization mostly followed the theoretical prediction,^{3,25} highlighting the quite excellent air-stability of the developed products. Indeed, the n-type SWNT films showed little degradation for at least three weeks (Figure S1). Additionally, such simple potential screening allowed the optimization of power factor (i.e. measure of power output, $\sigma\alpha^2$), approaching $500 \mu\text{W m}^{-1} \text{ K}^{-2}$ (Figure 1f).

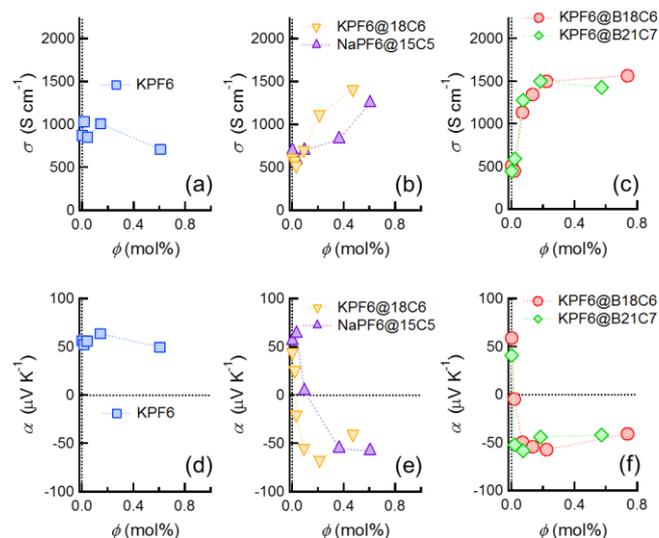


Figure 2. Thermolectric properties dependent on electrolytes. (a-c) Electrical conductivity and (e-g) the Seebeck coefficient of SWNT electrodes.

We then sought to evaluate molecular effects on the doping of SWNTs. Different supramolecular complexes such as sodium hexafluorophosphate (**NaPF₆**)/15-crown ether (**NaPF₆@15C5**) and **KPF₆**/benzo-18-crown ether (**KPF₆@B18C6**), along with **KPF₆** were only used as electrolytes, and compared to **KPF₆@18C6**. For quantitative analyses, we calculate the relative doping charge (ϕ , mol%):[‡]

$$\phi = \frac{Q}{F} \div \frac{m}{M} \times 100 \quad (1)$$

where Q is a doping charge (i.e. time-integrated electric currents), m is the mass of SWNT films, M is the molar mass of carbon (12 g mol^{-1}), and F is the Faraday constant ($96,485 \text{ C mol}^{-1}$). The observed thermolectric properties and polarity should be limited by prompt air-induced de-doping. Using this charge injection as an index, it is thus possible to compare the stability of each doped SWNTs.

In order to derive the importance of crown ethers, a controlled experiment with **KPF₆** was performed. The SWNT electrode exhibited no significant modulation of conductivity and the Seebeck coefficient after electrochemical reducing doping with **KPF₆**, drying and air-exposure (Figure 2a, d). This failure in conversion of SWNTs into n-type is presumably associated with the instability of ion pairs. In detail, charge

density mismatch between potassium ions (K^+) and delocalized negative charges in SWNTs could result in the degradation of n-type SWNTs (Scheme 1b). This result is in contrast with successful n-type doping with **KPF₆@18C6** in Figure 1.

We subsequently compare n-doping effects on the thermolectric performance of SWNTs with supramolecular electrolytes (e.g., **NaPF₆@15C5** and **KPF₆@18C6**). The injection of same charge amounts resulted in the formation of n-type SWNTs with different properties; **KPF₆@18C6** electrolytes enabled more efficient doping with a larger increase in conductivity. Furthermore, we observed the earlier appearance of negative Seebeck coefficients in comparison with **NaPF₆@15C5** (Figure 2b, e). These results indicate the importance of positive ions of electrolytes for controlling the electrochemical n-type doping of SWNT films.

Table 1. Charge amounts required for polarity inversion (ϕ_{min}).

| Electrolytes | ϕ_{min} (mol%) ^[a] |
|------------------------------|-------------------------------------------|
| KPF₆ | N.D. |
| TMAPF₆ | 0.08 |
| TBAPF₆ | 0.05 |
| NaPF₆@15C5 | 0.10 |
| KPF₆@18C6 | 0.03 |
| KPF₆@B18C6 | 0.02 |
| KPF₆@B21C7 | 0.01 |

[a] Data were obtained from Figure 2.

It should be noted that supramolecular electrolytes composed of benzo-crown ethers (**KPF₆@B18C6** and **KPF₆@B21C7**) promote the sign inversion of the Seebeck coefficient with fewer electrochemical charges (Figure 2c, f). Less than 0.2 % relative doping charges afforded the conductivity of $\sim 1500 \text{ S cm}^{-1}$ with the Seebeck coefficient of $\sim -60 \mu\text{V K}^{-1}$. This doping was more efficient than doping with conventional electrolytes, including tetramethylammonium hexafluorophosphate (**TMAPF₆**) and tetrabutylammonium salts (**TBAPF₆**) (See supporting information, Figure S2). We now consider the minimum doping charge (ϕ_{min}) required for turning the Seebeck coefficient negative, as an index for the efficiency of n-type doping. The trend of ϕ_{min} with different cations ($\text{K}^+ \gg \text{Na}^+ @15\text{C5} > \text{TMA}^+ > \text{TBA}^+ > \text{K}^+ @18\text{C6} > \text{K}^+ @\text{B18C6} > \text{K}^+ @\text{B21C7}$) suggests that larger cations promote efficient n-type doping (Table 1). **KPF₆@B21C7** showed indeed eight times better efficiency of n-type electrochemical doping than ordinary electrolytes such as **TMAPF₆**.

The present n-type characteristics of SWNTs are likely to originate from the balance between the electrochemical n-type doping and backward auto-oxidation. The n-type SWNTs coordinated with the crown ether complexes as charge compensating cations have shown relatively high stability toward auto-oxidation under ambient condition.¹⁶ More recently, Ferguson *et al.* have also reported that semiconducting SWNT networks functionalized with crown ether salts exhibit a minor drop in the negative Seebeck coefficient upon air-exposure, and highly air-stable n-type transport.¹⁸ The stabilization of the n-doped state of SWNTs

with the cation-crown ether complexes is thus responsible for the suppressed auto-oxidation activity and efficient electrochemical n-doping with the smaller ϕ_{\min} values.

The absorption spectra in Figure 1b revealed that the S_{11} transition was effectively quenched by doping but the second one (S_{22}) was mostly preserved after the electrochemical n-doping. This indicates the SWNTs are in the shallowly n-doped state with the Fermi level shift less than 0.2 eV. On the other hand, *in-situ* spectro-electrochemistry in Figure 3 (a) clarified that the S_{22} transition was quenched at -1 V. This is consistent with the energy gap between the first and second van Hove singularity points. Additionally, this potential is deep enough for efficient n-type doping. The S_{22} band, however, readily recovered under the open-circuit condition. This can be repeated several times without substantial degradation (Figure 3b). These results clearly indicate that the auto-oxidation induces the backward de-doping of n-type SWNTs from the second van Hove singularity level to the first one, although the shallow n-type states can be preserved after air-exposure by choosing appropriate counter cations.

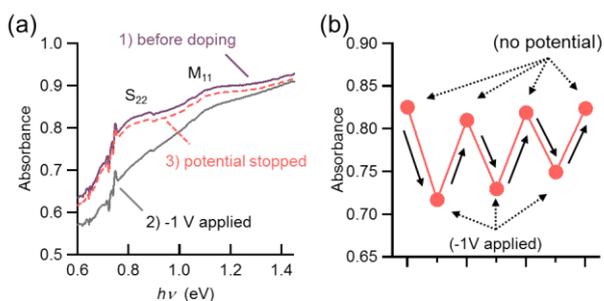


Figure 3. Spectroelectrochemistry. Absorption spectra of a SWNT electrode before and after *in-situ* electrochemical doping in acetonitrile with 0.1 M KPF₆@18C6; (1) before doping; (2) during doping at -1 V; and (3) after stopping potential application. (b) Sequential S_{22} absorption (0.82 eV) change upon a potential application.

Conclusions

In conclusion, we have quantitatively evaluated the n-type doping of SWNTs by electrochemical charging. Electrochemistry with supramolecular electrolytes was used for the preparation of stable n-type SWNT thin films and bulk materials. The molecular structures of electrolytes, particularly cations, indeed play a striking role in the n-type doping efficiency and the stability of n-doped state. Primary approaches to molecular doping with designed counter ions started in the 1980s in the field of conducting polymers.²⁶⁻²⁸ And now, supramolecular electrolytes can be applied in doping, enabling the modulation of n-type SWNTs thermoelectrics exhibiting unprecedented air-stability.

Conflicts of interest

There are no conflicts to declare.

Acknowledgement

We thank Prof. Leigh McDowell (NAIST) for his English proofreading of the whole manuscript. We thank Takuya Kitano (NAIST) for help with the SEM measurements. We thank financial supports from JST PRESTO grant number JPMJPR16R6. This work made use of NAIST common facilities supported by MEXT Nanotechnology Platform program.

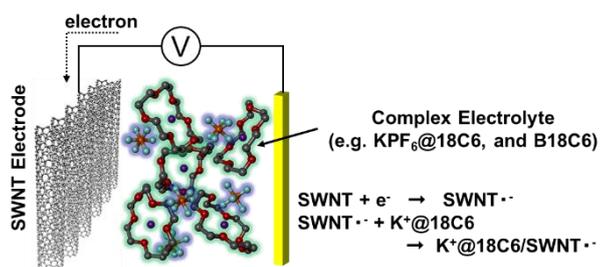
Notes and references

‡ The current profile could involve two phenomena: fast charging derived from electric double layer (EDL) formation on SWNTs, and the injection of charged carriers contributing to transport properties. In this paper, we integrated the whole chronoamperometry profiles for evaluating injected charges. The stabilization of n-type SWNTs could be associated with their complexation with counter cations, and such complexation and charge compensation are assisted by the EDL. Thus, all integrated charge amounts reflect whole stabilized doping phenomena including the both EDL and carrier charging.

- O. Bubnova, Z. U. Khan, A. Malti, S. Braun, M. Fahlman, M. Berggren, X. Crispin, *Nat. Mater.* **2011**, *10*, 429-433.
- B. Russ, A. Glaudell, J. J. Urban, M. L. Chabiny, R. A. Segalman, *Nat. Rev. Mater.* **2016**, *1*, 16050.
- A. D. Avery, B. H. Zhou, J. Lee, E.-S. Lee, E. M. Miller, R. Ihly, D. Wesenberg, K. S. Mistry, S. L. Guillot, B. L. Zink, Y.-H. Kim, J. L. Blackburn, A. J. Ferguson, *Nat. Energy* **2016**, *1*, 16033.
- G. J. Snyder, E. S. Toberer, *Nat. Mater.* **2008**, *7*, 105-114.
- O. Bubnova, M. Berggren, X. Crispin, *J. Am. Chem. Soc.* **2012**, *134*, 16456-16459.
- A. M. Glaudell, J. E. Cochran, S. N. Patel, M. L. Chabiny, *Adv. Energy Mater.* **2015**, *5*, 1401072.
- K. Shi, F. Zhang, C. A. Di, T. W. Yan, Y. Zou, D. Zhu, J. Y. Wang, J. Pei, *J. Am. Chem. Soc.* **2015**, *137*, 6979-6982.
- R. M. Ireland, Y. Liu, X. Guo, Y.-T. Cheng, S. Kola, W. Wang, R. Yang, M. L. Falk, T. Jones, H. E. Katz, *Adv. Sci.* **2015**, *2*, 1500015.
- D. Huang, H. Yao, Y. Cui, Y. Zou, F. Zhang, C. Wang, H. Shen, W. Jin, J. Zhu, Y. Diao, W. Xu, C.-a. Di, D. Zhu, *J. Am. Chem. Soc.* **2017**, *139*, 13013-13023; D. Yuan, D. Huang, C. Zhang, Y. Zou, C.-a. Di, X. Zhu, and D. Zhu, *ACS Appl. Mater. Interfaces* **2017**, *9*, 28795-28801.
- P. Wei, J. H. Oh, G. Dong, Z. Bao, *J. Am. Chem. Soc.* **2010**, *132*, 8852-8853.
- S. Guo, S. B. Kim, S. K. Mohapatra, Y. Qi, T. Sajoto, A. Kahn, S. R. Marder, S. Barlow, *Adv. Mater.* **2012**, *24*, 699-703.
- J. P. Small, K. M. Perez, P. Kim, *Phys. Rev. Lett.* **2003**, *91*, 256801.
- M. Shim, A. Javey, N. W. S. Kam, H. Dai, *J. Am. Chem. Soc.* **2001**, *123*, 11512-11513.
- a) T. Yasunishi, S. Kishimoto, Y. Ohno, *Jpn. J. Appl. Phys.* **2014**, *53*, 05FD01-1-5. b) T. Yasunishi, S. Kishimoto, E. I. Kauppinen, Y. Ohno, *phys. stat. sol. (c)* **2014**, *10*, 1612-1615.
- D. M. de Leeuw, M. M. J. Simenon, A. R. Brown, R. E. F. Einerhand, *Synth. Met.* **1997**, *87*, 53-59.
- Y. Nonoguchi, M. Nakano, T. Murayama, H. Hagino, S. Hama, K. Miyazaki, R. Matsubara, M. Nakamura, T. Kawai, *Adv. Funct. Mater.* **2016**, *26*, 3021-3028.
- R. G. Pearson, *J. Am. Chem. Soc.* **1963**, *85*, 3533-3539.
- 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. Holman Hughes, B. L. Zink, J. L. Blackburn, A. J. Ferguson, *Energy Environ. Sci.* **2017**, *10*, 2168-2179
- C. L. Liotta, H. P. Harris, *J. Am. Chem. Soc.* **1974**, *96*, 2250-2252.

- 20 a) C.-Z. Li, C.-C. Chueh, H.-L. Yip, F. Ding, X. Li, A. K. Y. Jen, *Adv. Mater.* **2013**, *25*, 2457-2461; b) C.-Z. Li, C.-C. Chueh, F. Ding, H.-L. Yip, P.-W. Liang, X. Li, A. K. Y. Jen, *Adv. Mater.* **2013**, *25*, 4425-4430.
- 21 R. Schlitz, F. G. Brunetti, A. M. Glauddell, P. L. Miller, M. Brady, C. J. Takacs, C. J. Hawker, M. L. Chabiny, *Adv. Mater.* **2014**, *26*, 2825-2830.
- 22 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.
- 23 S. A. Hodge, S. Fogden, C. A. Howard, N. T. Skipper, M. S. P. Shaffer, *ACS Nano* **2013**, *7*, 1769-1778.
- 24 Q. Zhang, E.H. Házroz, Z. Jin, L. Ren, X. Wang, R.S. Arvidson, A. Luttge, J. Kono, *Nano Lett.* **2013**, *13*, 5991-5996.
- 25 K. Yanagi, S. Kanda, Y. Oshima, Y. Kitamura, H. Kawai, T. Yamamoto, T. Takenobu, Y. Nakai, Y. Maniwa, *Nano Lett.* **2014**, *14*, 6437-6442.
- 26 M. Satoh, K. Kaneto, K. Yoshino, *Synth. Met.* **1986**, *14*, 289-296.
- 27 M. Yamaura, T. Hagiwara, K. Iwata, *Synth. Met.* **1988**, *26*, 209-224.
- 28 W. Wernet, *Synth. Met.* **1988**, *41-43*, 843-848.

Graphical Abstract



This paper describes a rational electrochemical method for selecting appropriate supramolecular dopants that convert p-type SWNTs to their n-type forms.