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Investigation of charge interaction between fullerene derivatives and single-walled carbon nanotubes

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Abstract
The charge interaction and corresponding doping effect between single-walled carbon nanotubes (SWNTs) and various fullerene derivatives, namely, C60, phenyl-C61-butyric acid methyl ester (PC61BM), methano-indenefullerene (MIF), 1',1",4',4"-tetrahydrodi[1,4]methanonaphthaleno[5,6]fullerene (ICBA), 1,4-bis(dimethylphenylsilylmethyl) [60]fullerene (SIMEF-1), and dimethyl(orthoanisyl) silylmethyl(dimethylphenyl-silylmethyl)[60]fullerene (SIMEF-2), are investigated. A variety of analytical techniques, including field-effect transistors (FETs) made of horizontally aligned arrays of SWNTs, is used as a means of investigation. Data from different measurements have to be used to obtain a concrete evaluation for the fullerene-applied SWNTs. The data collectively points toward the conclusion that fullerenes with high molecular orbital energy levels, namely, MIF, SIMEF-1, SIMEF-2, and PC61BM, induce p-type doping, while fullerenes with low molecular orbital energy levels, namely, ICBA and C60, induce n-type doping on the carbon nanotubes. Nevertheless, the SWNTs retained p-type characteristics because n-doping induced by the fullerenes are weak compared to the p-doping of the water and oxygen on carbon nanotubes. This means that fullerene derivatives have the ability to fine-tune the energy levels of carbon nanotubes, which can play a crucial role in carbon nanotube-based electronics, such as solar cells, light-emitting devices, and FETs.

KEYWORDS
doping, field-effect transistors, fullerene, single-walled carbon nanotubes, thin films

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INTRODUCTION

One-dimensional single-walled carbon nanotubes (SWNTs) show outstanding ballistic transport properties and unique geometry of an assembled network. In addition, SWNTs can possess different energy bands depending on their diameters and chirality, ranging from semiconducting to metallic.1,2 Such properties make SWNTs suitable for various device applications, specifically light-emitting displays, solar cells, and field-effect transistors (FETs).3,5 Their device applicability can be strengthened further by improving conductivity and controlling their energy levels by means of doping.6-8 There have been myriad methods reported for the p- or n-type chemical doping of SWNTs. The p-type doping involves using acids, for example, H2SO4,9-14 H2SO3,13 HNO3,7,10,14-22 HCl,10 SOCl2,11,21-27 CF3SO3H,28 and Nafion,29,30 as well as some oxidizing agents (= electron acceptors), such as tetrafluorotetracyano-p-quinodimethane,31-33 I2,11,34 IBr,34 PBr3,35 oxidizing agents (= electron acceptors), such as tetrafluorotetracyano-p-quinodimethane,31-33 I2,11,34 IBr,34 PBr3,35 bis(dicyanomethylene)quinoxaline,36 diimide,37,38 and BiOCl.39,40 The p-type dopants are generally reducing agents (= electron donors), namely, alkali metals (K-48-52 or Na-based dopants52), N2H4,22,53,54 aniline,11 polyamine,53 ethylene diamine,11 NH2,42 polymer PEI,55 viologen,56 3-(4-dimethylaminobenzylidene)-2-indolinone,57,58 and decamethylcobaltocene.59 Because of the challenging nature of the doping, the n-type dopants are less common than the p-type dopants. The intrinsic oxidation of SWNTs by water and oxygen in air makes SWNT stay p-doped.60-63

C60 and its derivatives have readily been used as organic electron acceptors in organic photoactive layers and as electron-transporting layers in perovskite solar cells.64-68 With the emergence of flexible and stretchable electronics, the number of reports on SWNT-based solar cells has increased dramatically in recent years.1,4 In one of the examples, SWNT films were used as both an anode and cathode, and the cathode SWNT film was soaked in phenyl-C61-butric acid methyl ester (PC61BM).56 PC61BM played a crucial role in controlling the energy level of the SWNTs. However, the exact mechanism of charge interaction and the doping were not discussed. Likewise, there has not been a conclusive study on the doping effect of fullerenes on SWNTs, but there have been many reports on photo-induced electron transfer from semiconducting SWNTs to C60.69-72 Therefore, it is absolutely paramount that we study the charge interaction between SWNTs and various fullerene derivatives without photo induction, and the resulting effect in terms of energetics.73-75

Here, we selected representative fullerene derivatives, namely, C60 methano-indenefullerene (MIF), 1,4-bis(dimethylphenyldimethyl)silylethynyl)[60]fullerene (SIMEF-1), dimethyl(orthoanisyl) silylmethyl(dimethylphenyldimethyl)[60]fullerene (SIMEF-2), 1′,1″,4′,4″-tetrahydrodi[1,4]methanonaphthaleno [5,6][fullerene (ICBA), and PC61BM.76-78 For the carbon nanotubes, aerosol-synthesized, free-standing SWNTs and horizontally aligned SWNTs (HA-SWNTs) were used for the analyses. For the charge interaction study, the Van der Pauw method of the four-probe measurement, Kelvin probe, photoelectron yield spectroscopy (PYS), Seebeck coefficient measurement, X-ray-induced photoelectron spectroscopy (XPS), Raman spectroscopy, visible-near infrared (Vis-NIR) absorbance measurements and FET characterizations were used. The results show that no one measurement can conclusively tell us about the charge interaction between the fullerene derivatives and SWNTs. There are many factors, such as intrinsically weak doping strength of the fullerenes on SWNTs and intermolecular interactions within the fullerenes, hindering the analysis. Only collective data from a variety of different measurements have to be used, which in this work demonstrated that MIF, SIMEF-1, SIMEF-2, and PC61BM induce p-doping on SWNTs, while ICBA and C60 induce n-doping. Despite discrepancies in some measurements, there is overwhelming evidence that the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of the fullerenes govern the doping characteristics. The higher the molecular orbital energy levels, the more likely they induce p-type doping. However, in spite of the n-doping effect by certain fullerenes, SWNTs in the atmosphere still remained slightly p-doped on account of the oxidation by oxygen and moisture in the air. This work uncovers the effect of fullerene derivatives on SWNT in terms of energetics and electronic properties. Although the doping effect is marginal, it is possible to tune the energetics of SWNTs using fullerenes, which will benefit greatly in designing high-performance SWNT-based electronics.

RESULTS AND DISCUSSION

Figure 1 shows the reported energy levels of metallic SWNTs with a chirality of (14,5),36 semiconducting-SWNTs with a (14,7) chirality,79 and the fullerene derivatives used in this work.76,80-82 It is important to differentiate the metallic SWNTs (m-SWNTs) from the semiconducting SWNTs (s-SWNTs) as SWNTs can have mixtures of m-SWNTs and s-SWNTs.83 The Schottky barriers between m-SWNTs and s-SWNTs have to be considered when investigating the doping effect.84,85

Sheet resistance measurement is one of the methods used for assessing the electrical property change upon doping. Figure 2A shows relative sheet resistance changes of SWNT films after a 10 mg mL−1 solution of fullerene was spin-coated (Tables S1 and S2). Application of fullerene derivatives showcases small decreases in the relative sheet resistance in all cases except C60. Application of C60
actually increased the relative sheet resistance, indicating n-doping. The relative decrease in the sheet resistance is the greatest for MIF, implying the strongest p-doping. We can infer that neither electron affinity nor crystallinity affected the relative sheet resistance change because there are no strongly electronegative atoms in the fullerene derivatives. In addition, MIF and C_{60}, both of which are small fullerenes, showed a totally different trend, whereas SIMEF-1 and SIMEF-2, which show different packing properties, showed similar doping effects.

The energy levels of a pristine SWNT film and fullerene-applied SWNT films were measured using the Kelvin probe and PYS (Figure 2B). For semiconducting materials, the Kelvin probe and PYS measurement values represent Fermi levels and valence levels, respectively, whereas in the case of conductive materials, both the Kelvin probe and PYS are supposed to give the same value as the Fermi level lies within either the conduction band or the valence band. The pristine SWNTs show the Kelvin probe and PYS values of −5.0 eV and −5.05 eV, respectively. The difference of 0.05 eV is negligible, and those values can be interpreted as the same Fermi level. By considering the difference of the Kelvin probe and PYS values within 0.1 eV to be negligible, we can deduce that, except ICBA, the fullerene-applied SWNTs all manifest p-type conductors. Among the samples, the MIF-applied SWNTs show the strongest p-doping effect, which is in agreement with the sheet resistance measurement. The data of the ICBA-applied SWNTs are difficult to interpret as the PYS measurement value (ca. −4.93 eV) is much higher than the Kelvin probe measurement value (ca. −5.12 eV).

The evaluation of Seebeck coefficients (given by \( S = \Delta V/\Delta T \)) can provide further information about the nature of doping. Figure 3 shows that the Seebeck slopes of the SWNTs are positive, manifesting a p-type characteristic due to the oxidation by water and oxygen. From the gradient change of the slopes, we can infer the type of doping effect and the degree of doping the fullerene induces. It is clear that, except ICBA and C_{60}, the other fullerenes induced p-type doping. Again, MIF induced the greatest p-doping as evidenced by the slope gradient. ICBA and C_{60} decreased the Seebeck coefficients, implying n-type doping.

Raman spectroscopy was used to identify the doping effect from the G and 2D bands of the fullerene-applied SWNT samples. Figures S1 and S2 show the G and 2D bands, respectively, of the fullerene-applied SWNTs. The
initial measurement (using 10 mg mL\(^{-1}\)) did not show clear trends among the samples. All the peaks were shifted to lower Raman shifts, ascribed to the overlap of the G and 2D bands from fullerenes. In fact, this explains the seemingly \(n\)-type doping of PC\(_{61}\)BM on SWNT in our previous report, which is not accurate in hindsight.\(^6\) To minimize the influence of the fullerenes, we lowered the fullerene concentration by 10 times (1 mg mL\(^{-1}\)). The G and 2D bands of low concentration of fullerenes-applied SWNTs displayed much clearer trends. From the quasilinearity plot (\([\Delta \omega_{2D}/\Delta \omega_{G}]_{\text{hole}} = 0.75 \pm 0.04\)) of the two fullerene concentrations, we can see that the low concentration and high concentration do not align, indicating that lowering the concentration does not weaken the doping effect (Figure S3).\(^8\) Therefore, a meaningful conclusion could only be drawn from the G and 2D bands of the low concentration of fullerenes-applied SWNTs. \(p\)-doping shifts the band to the right (higher Raman shift), and \(n\)-doping shifts the band to the left (lower Raman shift). Figure 4A shows that the G bands of the low concentration of the fullerene-applied SWNTs are shifted in the order of MIF > SIMEF-1 > SIMEF-2 > PCBM > ICBA \(\approx\) C\(_{60}\). The 2D bands are trickier to interpret as the difference is finer, and all the peaks are left-shifted because of the influence of the fullerene core. The 2D band shift trend is SIMEF-1 = MIF = SIMEF-2 > PCBM > ICBA \(\approx\) C\(_{60}\) (Figure 4B). Despite the slight discrepancy, the general trend is similar to those of the previous measurements.

XPS measurement can provide binding energy information of carbon atoms in SWNTs. Brønsted acid \(p\)-doping of SWNTs has been reported to decrease the energy of the C1s because the Fermi level lies further from the valence band edge on \(p\)-doping.\(^{10,90}\) We ran XPS on the fullerene derivative-applied SWNT films (Figure 5A). However, all the peaks exhibited higher binding energy than that of the pristine SWNTs. This is because XPS was used to measure C1s of the fullerene derivatives.\(^9\) Figure 5B shows the XPS C1s peaks of only the fullerene derivatives. It is clear that the C1s peaks of the fullerene derivatives possess relatively high binding energy. We estimated the C1s peak positions of the fullerene-applied SWNTs by subtracting the corresponding fullerene binding energy. Table S3 shows the calibrated C1s peak positions of the fullerene-applied SWNTs. Although the degree of doping does not agree with the previous outcome because of the inaccuracy of the calibration, the binding energy difference between the calibrated binding energies from that of the pristine SWNTs clearly shows that ICBA and C\(_{60}\) are the only two fullerenes inducing \(n\)-doping.

Vis-NIR absorbance spectroscopy of SWNT is a useful method for observing doping effects as \(p\)-type doping is accompanied by the suppression of the Van Hove transitions. We prepared samples with high and low concentrations of the
fullerene derivatives. Nonetheless, it was difficult to observe the suppression difference of the typical S11, S22 (s-SWNTs) and M11 (m-SWNTs) transition peaks in either concentration (Figure S4). We ascribed this to the mild doping effect of the fullerene derivatives.

The results of the analyses carried out up to this point are summarized in Table 1. Despite some discrepancies among the analytical techniques, the general trend of the doping follows that the molecular orbital energy levels of the fullerene derivatives are a dominant factor in inducing the doping effect.

Horizontally aligned SWNTs between two gold electrodes on a 100 nm-thick insulator-coated p-type silicon substrate (HA-SWNT FETs) were used to investigate the doping effect further (Figure 6A). In this setup, the measurements were made in air by applying a gate voltage (V_G) from −10 V to +10 V and then from +10 V to −10 V while measuring the drain current (I_DS) with a fixed drain voltage (V_DS) of −1 V. The negative V_G values mean that the SWNTs are positively charged by holes, whereas the positive V_G values mean that the SWNTs are negatively charged by electrons. HA-SWNT FETs can provide data of mixed SWNTs (Figure 6B) and s-SWNTs only by selectively burning off m-SWNTs using high voltage for the latter (Figure 6C). Previously, researchers used SWNT FETs to investigate charge transfer between fullerene and SWNTs. For example, Li et al showed that carbon peapods display a photo-induced electron transfer from encapsulated C60 to SWNTs, exhibiting p-type characteristic on illumination.92-100 Park et al reported thermally deposited C60 on SWNTs resulting in ambipolar SWNT FETs and a left shift of the threshold voltage, which became stronger with the increasing thickness of the deposited C60.101 Here, we demonstrate HA-SWNT FET analysis when various fullerene derivatives are solution-coated in air and the interaction with the mixed

![Figure 5](image_url) X-ray-induced photoelectron spectroscopy measurement of C1s peak of A, single-walled carbon nanotube films coated with fullerene derivatives solutions and B) fullerene derivatives alone

**TABLE 1** Summary of the doping analyses of the fullerene derivatives-applied single-walled carbon nanotubes conducted by various analytical techniques

| Fullerenes | Sheet resistance | Fermi level | Seebeck coefficient | Raman G-band | 2D-band | XPS | Vis–NIR |
|------------|------------------|-------------|---------------------|--------------|---------|-----|---------|
| MIF        | +++              | +++         | +++                 | ++           | +       | +0.08 eV | n/a     |
| SIMEF-1    | +                | +           | +                   | ++           | +       | +0.18 eV |         |
| SIMEF-2    | +                | +           | +                   | +            | +       | +0.05 eV |         |
| ICBA       | +                | n/a         | −                   | −            | −       | −0.1 eV  |         |
| PC61BM     | +                | +           | ++                  | −            | −       | −0.02 eV |         |
| C60        | −                | −           | −                   | −            | −       | −0.03 eV |         |

**Note:** Blue with “+” represents a p-doping trend, and red with “−” represents an n-doping trend.

**Abbreviations:** ICBA, 1’,1”,4’,4”-tetrahydro[1,4]methanonaphthalene[5,6]fullerene; MIF, methano-indenefullerene; SIMEF-1, 1,4-bis(dimethylphenylsilylmethyl)[60]fullerene; SIMEF-2, dimethyl(orthoanisyl) silylmethyl(dimethylphenylsilylmethyl)[60]fullerene; XPS, X-ray-induced photoelectron spectroscopy.
SWNTs and the s-SWNTs by a simple process of m-SWNT removal using high current, both of which have not been reported to date.

Each threshold gate voltage $V_{TH}$ of HA-SWNT-FETs was evaluated by extrapolation of the linear region method using Equation (1)\textsuperscript{102}:

$$V_{TH} = V_{Ge} - \frac{V_{DS}}{2} = V_{Ge} + 0.5$$

where $V_{Ge}$ is the gate voltage obtained by the linear extrapolation as shown in Figure S5. The HA-SWNT FET data show strong hysteresis arising from the trapped charge (Figure S6 and Table S4) attributed to the sp$^3$ defects on the SWNT walls\textsuperscript{103} which come from atmospheric $H_2O$\textsuperscript{60-62} $O_2$\textsuperscript{62,63} and hydroxyl groups on the dielectric surface of SWNTs\textsuperscript{104}. Thus, the obtained $V_{TH}$ values are different depending on the $V_G$ sweep directions, which include hole conduction for the increasing $V_G$ and electron conduction for the decreasing $V_G$. Therefore, the doping effect was interpreted by looking at the $V_{TH}$ shifts before and after the fullerene application, with the consideration of both increasing and decreasing $V_G$ (Figure 6B). The integrated results point to the same conclusion: ICBA and C$_{60}$ induce $n$-doping, while the other fullerenes induce $p$-doping on SWNTs (Table 2).

Purely semiconducting HA-SWNT FETs can give data with a high ON-OFF ratio, which translates to a more accurate doping effect observation. Semiconducting HA-SWNT FETs were achieved by electrically burning off m-SWNTs with the drain voltage up to $V_{DS} = 40$ V prior to the measurement\textsuperscript{105-107} Figure S7 and Table S5 show that the FET transfer characteristics demonstrate unipolar transport properties. Contrary to those from the mixed SWNTs, right shifts were dominant for the semiconducting HA-SWNT FETs after the fullerene application (Figure S7). By observing the $V_{TH}$ changes, we can infer that all of the fullerene derivatives except C$_{60}$ induce the $p$-doping effect.

The charge carrier mobility of a single string of SWNT can be determined from FET transfer characteristics in the linear region using Equation (2)\textsuperscript{108}:

$$\mu = \frac{L}{WC_i |V_{DS}|} \times g_m$$

where $L$ is the length of the SWNT channel (10 μm); $g_m = \frac{\partial I_{DS}}{\partial V_{GS}}$ is the transconductance at the threshold gate voltage; $W$ is the width of the SWNT channel, which is approximately 10 μm from the scanning electron microscopy (SEM) image (Figure S8); and $C_i$ is the capacitance, which is Equation (3)\textsuperscript{108}:

$$C_i = \frac{1}{A_0} \left[ C_Q^{-1} + \frac{2}{\pi} \ln \left( \frac{A_0}{\pi R} \sinh \left( \frac{2\pi d}{A_0} \right) \right) \right]^{-1}$$

where $A_0$ is the average distance between each nanotube (ca. 500 nm from Figure S8), $C_Q$ is the quantum capacitance value (4.0 \texttimes 10$^{-10}$ F m$^{-1}$)\textsuperscript{109}; $\epsilon$ is the dielectric constant (1 F m$^{-1}$ in air), $R$ is the radius of an SWNT (∼0.7 nm), and...
**Table 2** Doping trends of fullerene derivatives-applied single-walled carbon nanotubes (SWNTs) from the $V_{TH}$ data of HA-SWNT-FETs (mixed SWNTs and s-SWNTs) performed in this study

| Fullerenes   | Threshold voltage, $V_{TH}$ | Mixed SWNTs | s-SWNTs | Combined | Mixed SWNTs | s-SWNTs | Combined |
|--------------|-----------------------------|-------------|---------|----------|-------------|---------|----------|
| $V_G$ sweep (V) |                | -10 | +10 | +10 | -10 | +10 | -10 | Combined |
| MIF          | +               | +   | ++   | +   | +   | +   | ++   | Combined |
| SIMEF-1      | -               | +   | +    | +   | +   | +   | ++   | Combined |
| SIMEF-2      | +               | +   | ++   | +   | +   | +   | ++   | Combined |
| ICBA         | -               | +   | -    | n/a | +   | +   | ++   | Combined |
| PC61BM       | -               | +++ | ++   | +   | +   | +   | ++   | Combined |
| C60          | -               | +   | n/a  | -   | -   | -   | -     | Combined |

Note: Blue with “+” represents a p-doping trend, and red with “−” represent an n-doping trend.
Abbreviations: ICBA, 1',1'',4',4''-tetrahydrodi[1,4]methanonaphthaleno[5,6]fullerene; MIF, methano-indenefullerene; SIMEF-1, 1,4-bis(dimethylphenylsilylmethyl)[60] fullerene; SIMEF-2, dimethyl(orthoanisyl) silylmethyl(dimethylphenylsilylmethyl)[60]fullerene; SWNT, single-walled carbon nanotubes.

$d$ is the thickness of dielectric gate (100 nm of SiO2 layer).
After calculation, $C_i \approx 8.00 \times 10^{-6}$ F is found. Therefore, Equation (2) can be calculated as the following:

$$\mu = \frac{L}{W C_{CNT}|V_{DS}|} \times g_m \approx 1.25 \times 10^5 \times g_m$$

The calculated mobilities of SWNTs before and after the fullerene application are shown in Figure S9. Surprisingly, there was no significant trend in the mobility among the different fullerene derivatives for both the mixed HA-SWNT FETs and semiconducting HA-SWNT FETs (Table S6).

Figure 7 illustrates the charge transfer mechanism in the SWNTs. SWNTs in air are inevitably p-doped by oxygen...
and water (Figure 7A). With the presence of fullerenes, charge transfer can occur between the fullerenes and SWNTs. The direction and degree of the charge transfer depend on the HOMO and LUMO levels of the fullerene (Figure 1). For example, in the case of C₆₀, electrons will transfer from C₆₀ to SWNTs as C₆₀ induces n-doping (Figure 7B). However, SWNTs still remain p-doped because fullerene-induced doping effects are found to be mild. When these fullerene-applied SWNTs are used as electrodes in devices, such as perovskite solar cells, excitons will be generated, and either electrons or holes will transfer to the SWNT electrodes (Figure 7C). Being a p-type conductor, SWNTs are more inclined to accept holes than electrons, functioning as an anode. From the energy diagram, which includes CH₃NH₃PbI₃ (MAPbI₃) and HC(NH₂)₂PbI₃ (FAPbI₃), we can deduce what kind of charge transfer may occur (Figure S10). Fullere derivatives with strong p-doping ability, such as MIF, would shift the Fermi level of SWNTs down. In addition, LUMO of MIF (−5.5 eV) aligns well with the valence level of the perovskite materials (−5.3 eV for MAPbI₃ and −5.6 eV for FAPbI₃), which implies that the application of MIFs will enhance the performance of SWNTs as an anode. On the other hand, the application of C₆₀ will make SWNTs cathodes by bringing the Fermi level closer to the HOMO of C₆₀ (−3.95 eV) and the conduction band of the perovskite layers (−3.95 eV for MAPbI₃ and −4.20 eV for FAPbI₃) (Figure 7D).

3 | CONCLUSION

We investigated the charge transfer between SWNTs and the fullerene derivatives using various analyses. Due to the complexity of the system, no single measurement could provide a conclusive outcome. Collective evidence had to be put together to derive a valid conclusion. It was found that the fullerene derivatives induce charge transfer depending on their HOMO and LUMO levels. Fullerene derivatives with high HOMO and LUMO levels induce stronger p-doping than those with low HOMO and LUMO molecular energy levels, while mild n-doping was observed in the case of ICBA, and C₆₀. If we look at the p-doping trend, it is MIF > SIMEF-1 > SIMEF-2 > PC₆₁BM < ICBA > C₆₀. From the trend of HOMO, it is MIF > SIMEF-1 = SIMEF-2 > ICBA = PC₆₁BM > C₆₀. This means that the HOMO trend follows the doping trend, which makes sense as the hole movement from fullerene to SWNT can be speculated to be hindered by the energetic barrier between the HOMO of fullerene and the energy level of the SWNTs. The similar HOMO levels between SIMEF-1 and SIMEF-2, and between ICBA and PC₆₁BM, beg a different explanation. By looking at the trend of the LUMO level, we can hypothesize that the LUMO also influences the strength of the doping effect. The different doping effect between SIMEF-1 and SIMEF-2 can be thought to arise from the difference in the LUMO levels. The strong electron affinity of fullerene is thought to p-dope SWNT. However, having a high energy barrier between the LUMO of fullerene and the energy level of SWNTs can hinder the electron transfer, which leads to a reduced doping effect. The same is true for the difference between ICBA and PC₆₁BM, in which the higher-lying LUMO of ICBA is suspected to weaken the p-doping. Therefore, we can say that the HOMO and LUMO levels of fullerene are thought to govern the doping behavior. Other factors, such as crystallinity, size, and electronegativity of fullerenes, did not play an important role in the charge interactions. This finding demonstrates that fullerenes can be used as mild dopants and energy level tuners for the carbon electrodes. It serves as a guideline for systems, in which carbon electrodes, such as SWNTs, and fullerenes are used together by providing an insight into the charge interaction and corresponding doping effect.

4 | EXPERIMENTAL SECTION

4.1 | SWNTs preparation for conductive films

SWNTs were synthesized by an aerosol (floating catalyst) CVD method based on ferrocene vapor decomposition in a CO atmosphere. The catalyst precursor was vaporized by passing room temperature CO through a cartridge filled with ferrocene powder. Ferrocene vapor was then introduced into the high-temperature zone of a ceramic tube reactor through a water-cooled probe and mixed with additional CO. To obtain stable growth of SWNTs, a controlled amount of CO₂ was mixed with the CO carbon source. SWNTs were directly collected at the downstream of the reactor by filtering the flow through a nitrocellulose membrane filter (Millipore Corp; HAWP, 0.45 μm pore diameter). These films were supplied on a large nitrocellulose membrane with 80% transparency (evaluated at 550 nm wavelength).

SWNTs on a nitrocellulose membrane were dried-transferred onto glass substrates, followed by ethanol application. Then, the samples were annealed at 100°C for 10 minutes and left in a vacuum for at least 12 hours.

4.2 | SWNTs growth for HA-SWNT-FETs

R-cut quartz was used for aligned growth. The quartz substrates were annealed at 900°C in air for 12 hours. An Fe catalyst (0.2 nm thick) was photolithographically patterned into parallel stripes using thermal evaporation, followed by a liftoff and heating at 500°C in air. SWNTs were grown at 800°C using ethanol as a feedstock gas.
4.3 | Electrode patterning for HA-SWNT-FETs

Electrodes (Ti/Pt, typically 2 nm/23 nm) were photolithographically patterned on as-delivered silicon substrates (SUMCO Corp., highly p-doped Si with 100 nm-thick oxide layer) by sputtering. A photoresist layer and thin metal layers were used to obtain electrodes with smooth edges. Here, p-doped silicon substrates functioned as a global back gate.

4.4 | SWNTs transfer for HA-SWNT-FETs

A 4 wt% of poly(methyl methacrylate) (PMMA) in anisole was spin-coated at 2000 rpm on quartz substrates, on which SWNTs were grown, followed by heating at 170°C in air for 15 minutes. After scratching the edges using a diamond knife, the substrates were immersed in aqueous KOH (1 mol L⁻¹) and heated at 100°C for 10 minutes. The PMMA thin films were spontaneously peeled from the substrate when placed in cold distilled water, which were then picked up by the target substrates with the prepatterned electrodes. After drying in air at room temperature, the substrates were heated at 170°C for 30 minutes. Finally, the PMMA films were dissolved in acetone, followed by annealing at 350°C in a vacuum for 3 hours.

4.5 | m-SWNT removal by Ohmic heating on HA-SWNT-FETs

m-SWNTs were burnt off by ramping the drain voltage from 0 V to a negative value until the drain current became sufficiently small (typically up to \( V_{\text{DS}} = -6 \text{ V \mu m}^{-1} \)), while a positive gate voltage \( (V_{\text{GS}} = 10 \text{ V}) \) was applied to turn the s-SWNTs off.

4.6 | Fullerene solution preparation and application

\( \text{C}_{60}, \text{PC}_{61} \text{BM}, \) and ICBA were purchased from Frontier Carbon. MIF, SIMEF-1, and SIMEF-2 were synthesized according to our previous reports. The fullerenes were dissolved in chlorobenzene at a concentration of 10 mg mL⁻¹ or 1 mg mL⁻¹ for the low-concentration doping analysis. The fullerene derivatives were spin-coated at 3000 rpm for 30 seconds on SWNT films or HA-SWNT-FETs, followed by annealing in air at 100°C for 10 minutes.

4.7 | Measurements of electronics properties

Sheet resistance of SWNT films was measured by using a Van der Paw method, which involves using four indium contacts pressed on the corners of SWNT films. Four-probe measurements were taken using an Analyzer Agilent 4156C, and the sheet resistance was determined using the Van der Paw equation. Kelvin probe force microscopy (Riken Keiki FAC-2) and PYS (Riken Keiki AC3) were used for energy level measurement. Absorbance measurements were performed using Shimadzu UV-3150. XPS measurements were carried out using a ULVAC PHI 5000 VersaProbe machine in high vacuum. Seebeck measurements were taken by a home-made system where SWNT films on glass were positioned to connect two copper sheets with carbon paste. Resistive heaters were attached on the hot side copper sheet, and T-type thermocouple was attached between hot and cold side copper sheets to measure the temperature gradient \( \Delta T \). Thermoelectric voltage \( (\Delta V) \) was measured between the two copper plates. The measurements of HA-SWNT-FETs were performed with three probes (for Source, Drain and Gate) using an Analyzer Agilent 4156C. SEM measurement was carried out on an S-4800 (Hitachi).

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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