

Reduction-Controlled Viologen in Bisolvent as an Environmentally Stable n-Type Dopant for Carbon Nanotubes

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Abstract: Various viologens have been used to control the doping of single-walled carbon nanotubes (SWCNTs) via direct redox reactions. A new method of extracting neutral viologen (V^0) was introduced using a biphasic system of toluene and viologen-dissolved water. A reductant of sodium borohydride transferred positively charged viologen (V^{2+}) into V^0 , where the reduced V^0 was separated into toluene with high separation yield. This separated V^0 solution was dropped on carbon nanotube transistors to investigate the doping effect of CNTs. With a viologen concentration of 3 mM, all the p-type CNT transistors were converted to n-type with improved on/off ratios. This was achieved by donating electrons spontaneously to CNTs from neutral V^0 , leaving energetically stable V^{2+} on the nanotube surface again. The doped CNTs were stable in water due to the presence of hydrophobic V^0 at the outermost CNT transistors, which may act as a protecting layer to prevent further oxidation from water.

1. Introduction

Although carbon nanotubes (CNTs) have shown highly efficient transistor performance such as high mobility and a large on/off ratio, they are naturally p-type semiconductors under ambient conditions.^{1–5} Typical n-type doping of CNTs with alkali metals has been achieved under a vacuum environment, but they are unstable in air.^{6–9} It is in general extremely difficult to produce environmentally stable n-type CNTs. Polymers containing electron-donating groups, typically amine-rich polymers such as poly(ethyleneimine) (PEI), have demonstrated relatively stable n-type doping effects.^{10–12} Nevertheless, the

stability in water and air has never been accessed to a reliable degree.¹³ Recently, the choice of metal electrodes with low work functions such as Al and Sc provided a new route of achieving n-type doping in CNTs.^{14,15} However, such electrode-controlled n-type doping often limits applications of CNTs to various integration units.^{16,17} The requirements of n-type dopants in CNTs are (i) efficient doping capability independent of CNT diameters and (ii) long-term stability under ambient conditions.

The doping of nanotubes by chemical dopants involves a direct redox reaction via charge transfer.¹⁸ The charge transfer alters the Fermi level and subsequently work function. The work function has been suggested as an important criterion in determining the p-type doping efficiency of the chemical dopant in CNTs.¹⁹ A similar principle can be applied to n-type doping. It is also important to realize that the reduction potential of CNTs is directly related to the work function which is diameter- and

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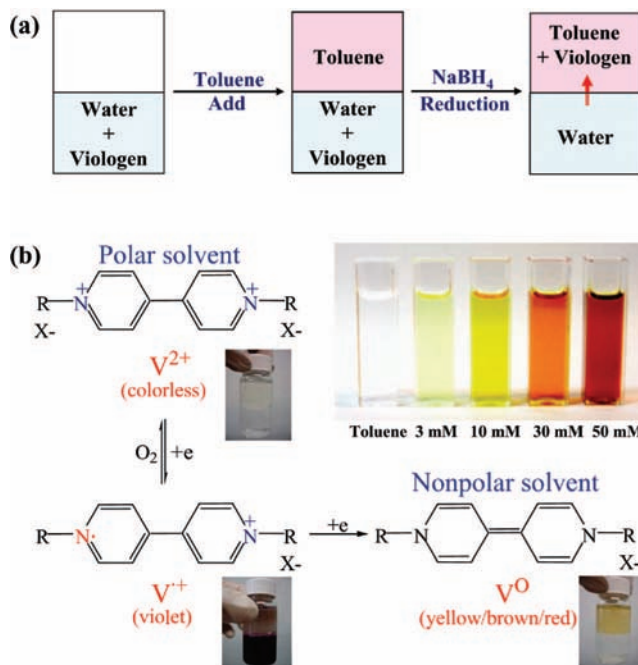
Table 1. Various Viologen Molecules: Nomenclature, Structure, and Reduction Potential

Sample name	Structure	Reduction potential	
		$E_1 (V^{2+} \rightarrow V^{+})$	$E_2 (V^{+} \rightarrow V^0)$
1,1'-Dibenzyl-4,4'-bipyridinium dichloride (BV)		-0.332 V	-0.790 V
Methyl viologen dichloride hydrate (MV)		-0.446 V	-0.880 V
Ethyl viologen diperchlorate (EV)		-0.449 V	N.A. ^a

^a N.A. (nonavailable).

chirality-dependent.^{20–22} It is well-known that viologen is a strong reducing agent and can be used as an electron relay molecule for many photochemical reactions.²³ Viologens have three oxidation states with distinct colors: colorless V^{2+} , violet V^{+} , and yellow V^0 . Viologen (V^0) is known to have a relatively low reduction potential vs standard hydrogen electrode (SHE) in Table 1.²⁴ This negative reduction potential is a measure of the extent to which viologen donates electrons. In the case of CNTs, the positions of conduction band edges are located near 0 V above the potential of the SHE in the CNT diameter range 1.37–1.7 nm.²¹ The lower reduction potential in the dopant gives rise to a better doping efficiency in the CNTs. Neutral viologen molecules are able to donate electrons to the CNTs with this diameter range; i.e., the CNTs are n-type doped. The relative potential levels rationalize the spontaneous electron transfer from the dopant (oxidation) to the nanotube (reduction).

This study has two goals. The first is to extract a neutral viologen solution with high separation yield from charged viologen molecules by using a reducing agent of sodium borohydride. The second is to use neutral viologen to invoke stable n-type doping in carbon nanotubes under ambient conditions. In this work, we chose various viologen molecules with different reduction potentials and different numbers of aromatic rings to control the n-type doping of CNTs. One advantage of viologen molecules is the controllability of their charged states, which is known as a reversible two-electron redox reaction.²⁵ A charged state of viologen, V^{2+} , was reduced by sodium borohydride in water to a neutral state of V^0 which was transferred separately to toluene, resulting in a toluene solution containing the reduced V^0 . This new design of the reducing process enabled us to extract the neutral viologen molecules separately in a nonpolar toluene solution from water with a separation yield of 100%. This solution was dropped onto the CNT transistors. By direct redox reaction, the neutral

**Figure 1.** (a) Schematic of preparation procedure of reducing viologen agent in bisolvent. (b) Two-electron redox reactions by reducing agent and the color dependence on the reduced viologen concentration.

V^0 molecules can be ionized spontaneously to V^{2+} by donating electrons to CNTs. This resulted in a stable n-type doping of CNTs. The long-term stability under ambient conditions was further tested.

2. Sample Preparation, Experimental Methods, and Theoretical Calculations

Three viologen molecules were chosen: 1,1'-dibenzyl-4,4'-bipyridinium dichloride (benzyl viologen: BV) with a purity of >96.0% from Fluka, ethyl viologen diperchlorate (ethyl viologen: EV) with a purity of 98%, and methyl viologen dichloride hydrate (methyl viologen: MV) with a purity of 98% from Aldrich, as listed in Table 1. The reduction potentials were also provided with chemical structures. The basic unit of viologen molecules is 4,4'-bipyridine with various ligands. Two nitrogen sites were positively charged in solvent, leaving a V^{2+} state.

0.04 mg of viologen powder was dissolved in 10 mL of water followed by an addition of 10 mL of toluene solution, resulting in the biphasic solution; one is a viologen-containing water solution, and the other is a toluene solution. Sodium borohydride (200 mM), as a catalytic reducing agent, was added to the biphasic solution as depicted in Figure 1a. The resulting biphasic solution was left for a day. As the reaction proceeded, a color change from yellow to red was observed in the separated toluene phase, depending on the initial concentration of viologen in water; this is because V^0 reduced by the sodium borohydride is hydrophobic and is transferred separately from the water phase to the toluene phase. 5 μL of the resulting toluene solution were dropped onto the CNT transistor at a time by using a micropipette. Each sample was dried under ambient conditions for 5 min.

The CNT thin film transistors (CNT-TFTs) were synthesized with an array of predesigned patterns of photoresist catalyst on a Si substrate covered with SiO_2 (thickness: 400 nm) using plasma-assisted chemical vapor deposition. The corresponding source and drain electrodes with Ti (10 nm)/Au (100 nm) (channel length: 10 μm , width: 40 μm) were deposited to form an array of 200 CNT-TFTs. The detailed method has been described elsewhere.²⁶ I - V characteristics of the CNT-TFTs were measured under ambient conditions by a source-measure unit (Keithley 236, 237) using a

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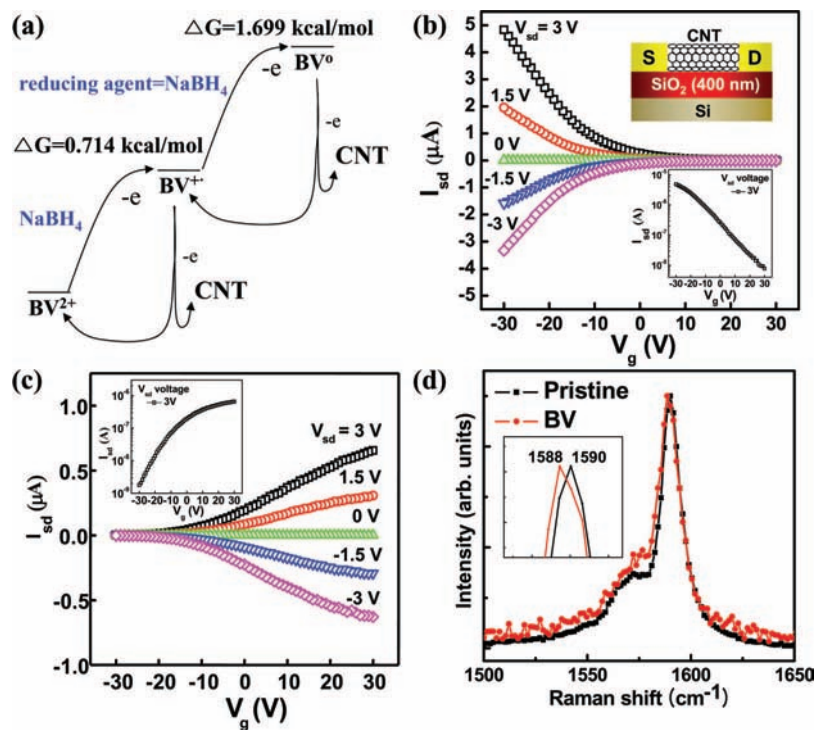


Figure 2. (a) Reversible redox reaction with Gibbs free energy difference. (b) Typical I - V characteristics of the pristine SWCNT-TFT channel. Inset: schematic of back gate CNT-TFT device. (c) I - V characteristics of benzyl viologen-treated TFTs (5 mM). (d) G-band of Raman spectra at an excitation energy of 2.41 eV of the pristine SWCNTs (diamond) and that of the BV-doped SWCNTs (circle).

probe station. An Ar⁺ ion laser (514 nm) was employed as a source of resonant Raman spectroscopy (Renishaw, microprobe RM1000-Invia). A Rayleigh line rejection filter with the spectral range 50–3200 cm⁻¹ for Stokes shift was used to characterize the SWCNTs. UV-vis-NIR absorption measurements were taken using a Cary 5000 spectrophotometer (Varian, CA, U.S.A.).

To understand our experimental observations, *ab initio* calculations were performed based on the density functional theory.²⁷ Wave functions were expanded in the pseudoatomic orbital basis set implemented in the OpenMX package. Norm-conserving Troullier–Martins pseudopotentials were employed.²⁸ For the exchange–correlation term, the Ceperley–Alder type local density approximation was employed, and the energy cutoff for real space mesh points was 90 Ry.²⁹ The binding energy was calculated by $E_b(\text{CNT-Vio}) = E_t(\text{CNT-Vio}) - E_t(\text{CNT}) - E_t(\text{Vio})$, where E_t is the total energy of a given system. The semiconducting (10,0) nanotube was chosen for our calculations. This clearly demonstrates how the band structure and the Fermi level can be modified with the adsorption of viologen.

3. Results and Discussion

Figure 1b represents a reduction procedure by a reducing agent. The dissolved viologen molecules in water, which are positively charged (V²⁺), were initially colorless. With an addition of NaBH₄, which is also colorless, the solution immediately turned to violet. This is evidence of formation of the cation radical (V^{•+}), as shown in the schematic. Since the generated V^{•+} molecules were still positively charged, they were dissolved in hydrophilic water (violet) at the bottom of the vial. After a few seconds, the color of the toluene solution changed

to yellow. This clearly demonstrates that neutral V⁰ was generated as a consequence of further reduction of V^{•+} to V⁰. Since the V⁰ molecules were neutral, they could no longer stay in hydrophilic water and instead were separated into nonpolar toluene. The supernatant toluene solution containing V⁰ viologen molecules was easily extracted by decanting. Figure 1b also shows the color dependence on viologen concentration. The color became darker with increasing viologen concentrations. This was confirmed by the absorption spectra, where the peak intensity at 405 nm was changed but no peak shift was observed with viologen concentration (see Supporting Information Figure S1).²³ This implies a high yield of selective separation of V⁰ in toluene. It is worth mentioning that bubbles of hydrogen gas were continually generated during the reduction reaction. This was ascribed to the chemical reaction of sodium borohydride with viologen molecules in water.³⁰ The bubble generation also assisted V⁰ in water to transfer into the toluene region.

When this solution was dropped onto CNTs, V⁰ molecules in the toluene region became oxidized by donating electrons to CNTs spontaneously and reached the V²⁺ state. This redox analyte undergoes a reversible two-electron redox reaction, as shown in Figure 2a. The large Gibbs free energy difference of 2.4 kcal/mol between BV²⁺ and BV⁰ prevents BV²⁺ from being reduced to BV⁰ under ambient conditions. This could be a clue to providing environmental stability in doped CNTs which will be discussed later. The CNT-TFT prepared by PECVD in Figure 2b showed a clear p-type behavior with back-gate modulation (high current at negative gate bias and no current at positive gate bias). With a single drop of V⁰ solution in 5 mM, the carrier type was converted from p-type (hole carrier) to n-type (electron

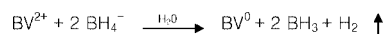
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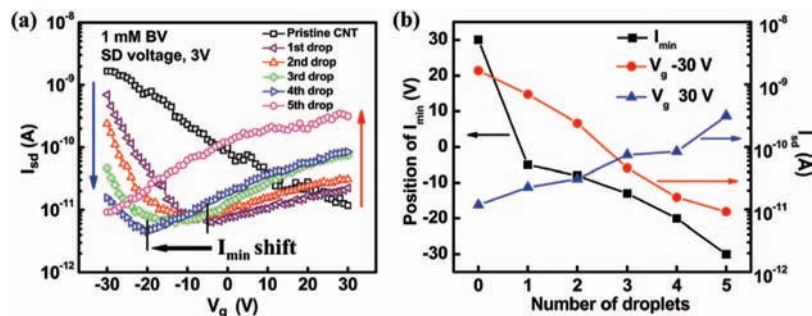


Figure 3. Controllability of n-type doping. (a) I – V characteristics in terms of number of BV droplets. Each drop of $5 \mu\text{L}$ had a concentration of 1 mM viologen, and (b) the corresponding parameters of I_{min} position and I_{sd} at a gate bias of -30 and 30 V .

carrier), i.e., high on-current at positive gate bias and small off-current at negative gate bias (Figure 2c). This is ascribed to the electron donation to CNTs during the charge state conversion of viologen from V^0 to V^{2+} . The development of a Breit–Wigner–Fano (BWF) component at the lower energy side of the G-band in Figure 2d is further evidence of charge accumulation in CNTs. The inset also indicates phonon softening of the G-band by 2 cm^{-1} , which is additional evidence of a Fermi level shift in CNTs.^{31,32}

Figure 3 shows the controllability of doping efficiency, which is essential in designing the mobility of various devices. In this case, 1 mM of BV was dropped onto the CNT-TFT. With an increasing number of droplets, the hole current at the negative gate bias decreased, while the electron current increased. Furthermore, the position of the minimum current was downshifted to the direction of the negative gate bias, as shown in Figure 3a. All these indicated a type conversion from the initial p-type to n-type in the TFT, and therefore the carrier concentration can be engineered.

Our first-principles calculations also confirm the n-type conversion with viologen doping. The adsorption (binding) energy of the neutral viologen molecule on the (10,0) CNT is about -2.5 eV . As shown in Figure 4b, the Fermi level is upshifted toward the conduction band minimum by nearly 0.3 eV , compared to the bare (10,0) CNT in Figure 4a. In addition, the viologen-related (filled) molecular states (V_1 and V_2) are located near -0.05 and -0.3 eV below the Fermi level. Figure 4c shows an isodensity surface plot of electron accumulation (red near CNT) and depletion (blue near viologen). This indicates that electrons are transferred from neutral viologen (V^0) to the CNT. Our Mulliken population analysis also shows that viologen donates electrons ($\sim 0.2 \text{ e}$) to the nanotube. This trend of electron donation to the CNT is in good agreement with the conversion of V^0 to V^{2+} . The precise amount of the donated electrons depends on the relative electronegativity of both species.

In addition to BV, we have also evaluated other n-type dopants such as MV and EV. These materials clearly demonstrated n-type doping, as expected (see the Supporting Information Figure S2). The on/off ratio was improved after n-doping, compared to the p-type pristine sample in the case of BV, whereas those of MV and EV were slightly reduced after n-doping (Figure 5a). This reduction of the on/off ratio in MV

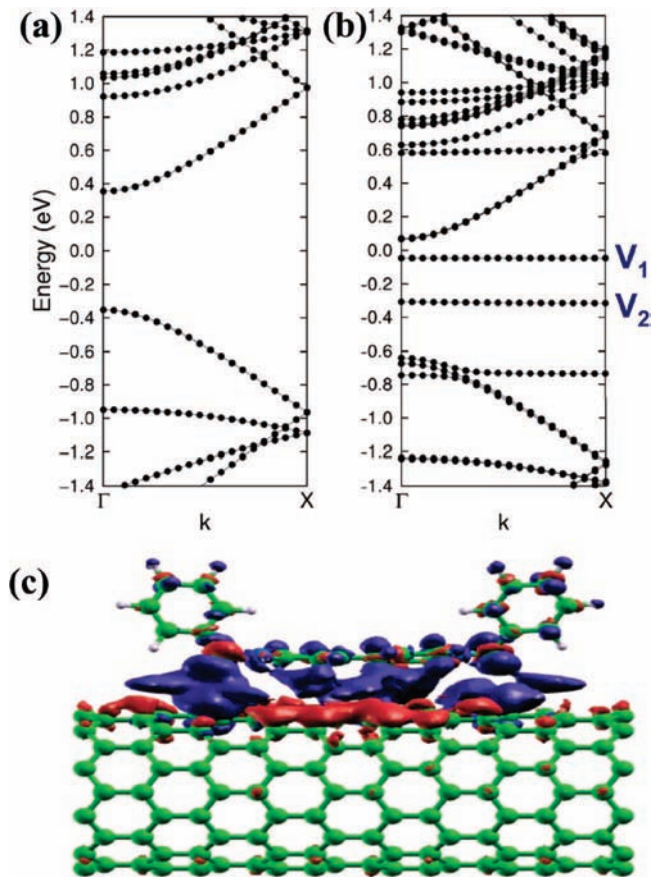


Figure 4. Band structures of (a) pure (10,0) CNT and (b) the neutral viologen-adsorbed (10,0) CNT. The Fermi level is set to zero. (c) Isodensity surface plot of electron accumulation (red) and depletion (blue). V_1 and V_2 indicate molecular states of viologen. The values for the red and blue surfaces in (c) are $\pm 0.025 \text{ e} \text{ \AA}^{-3}$.

and EV after n-doping originates from the large off-current compared to that of BV (Figure S2). Large off-current in the case of MV is strongly related to lower reduction potentials compared to the case of BV (see Table 1).³³ Although the reduction potential ($V^{++} \rightarrow V^0$) is not available from the literature, we can conjecture that its reduction potential is lower or similar to that of MV. This trend of large off-current and, in turn, a small on/off ratio is similar to that for the doping of poly(ethyleneimine) (PEI).^{10,33} We therefore conclude that BV seems to be the best n-dopant from a device point of view.

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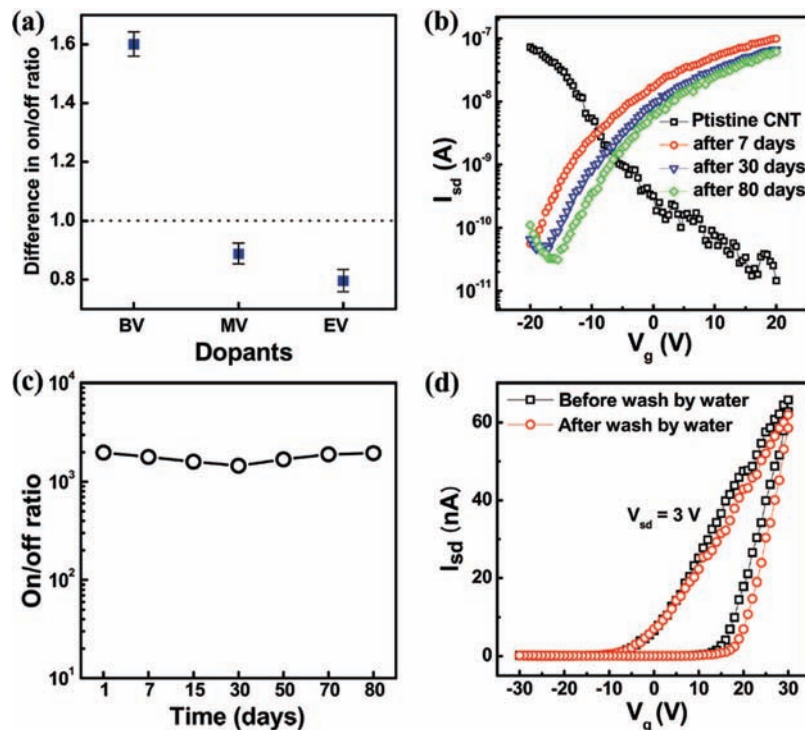


Figure 5. (a) Comparison of on/off ratios for various viologen-treated samples of BV, MV, and EV with respect to the on/off ratio of the pristine p-type samples. (b) Stability of I - V characteristics of BV-doped device exposed for up to 80 days under ambient conditions with one drop of 5 μ L of 50 mM concentration. (c) Variation of the on/off ratio as a function of exposure time under ambient conditions. (d) Stability of I - V characteristics of the BV-doped device similar to (b) and after soaking in water.

One critical issue in the n-type doping of CNT devices is the long-term stability under ambient conditions. Figure 5b shows the long-term stability of a 50 mM BV-doped device under ambient conditions. The on/off ratio was slightly reduced, but the n-type doping behavior was still preserved, even after 80 days of exposure. Figure 5c shows the on/off ratio change for 80 days under ambient conditions. It is remarkable to see that the on/off ratio remained almost constant during such long exposure. Another interesting point regarding BV doping is that the stability of the device was sustained even under harsh conditions. The transistor that was doped with 50 mM BV was soaked in water for a day. The I - V characteristics were not altered appreciably, as shown in Figure 5d. The stability of our device even with a water environment shown here could be a reason that the long-term stability under ambient conditions in Figure 5b was maintained. Some of the neutral viologen adsorbed directly on the CNT surface could be converted to V^{x+} by donating electrons to the CNTs, but other viologens adsorbed away from the CNT surface remained in a neutral state. These are hydrophobic and may act as a protecting layer to prevent further oxidation from the ambient.³⁴ These advantages of long-term stability will play an important role in applications of CNTs to numerous nanodevices.

4. Conclusions

We have demonstrated that viologen can be used as an efficient n-type dopant of CNTs. An efficient method of extracting neutral viologen molecules in bisolvent was designed. This solution was directly applied to doping CNT-TFTs. Clear n-type doping with BV was demonstrated with an improved on/off ratio compared to the p-type device. The long-term stability of BV under ambient conditions up to 80 days was demonstrated. The stability of the CNT-TFTs was maintained under severe conditions such as washing with water. This high stability of viologen originates from the hydrophobic nature of V^0 which may act as a protecting layer to prevent further oxidation from the ambient. We expect that our approach of n-type doping of CNTs will be useful for CNT-based nanoelectronics.

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Supporting Information Available: Figures S1 and S2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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