**Supporting Information**

# Efficient Dye-Sensitized Photovoltaic Wires Based on an Organic Redox Electrolyte

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## Experimental section

*Synthesis of 5-mercapto-1-methyltetrazole N-tetramethylammonium salt ($NMe_4^+T^-$).* It was synthesized by the neutralization of 5-mercapto-1-methyltetrazole (1.46 g, 12.6 mmol; Aladdin Chemistry, 98%) with a 10 wt% solution of tetramethylammonium hydroxide in methanol (13.7 mL). The reaction occurred at a $N_2$ atmosphere, and the mixture was then stirred at room temperature for 12 h. After removal of the residual organic solvent and drying at 40 $^oC$ in vacuum overnight, the resulting product was mixed with $P_2O_5$ to produce $NMe_4^+T^-$. The yield was 95%, and no impurities were detected by $^1H$ NMR.

$^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$ = 3.62 (s, 3H, $CH_3$), 3.10 (s, 12H, $NMe_4^+$).

*Synthesis of di-5-(1-methyltetrazole) disulfide ($T_2$).* It was synthesized from the oxidation of 5-mercapto-1-methyltetrazole (3.0 g, 25.8 mmol) by iodine (3.0 g, 11.9 mmol; Sinopharm, 99.8%) in water. The mixture was sonicated for 1.5 h until the powder $I_2$ disappeared. The white precipitate was then collected by filtration and washed with cold deionized water, followed by drying under vacuum at 40 $^oC$ for 24 h

to produce $T_2$. The yield was 68%, and no impurities were detected by $^1$H NMR. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 4.05 (s, 6H, $CH_3$).

*Fabrication of photovoltaic wire.* Perpendicularly aligned $TiO_2$ nanotube arrays were grown on Ti wires by electrochemical anodization in an ethylene glycol solution containing 0.3 wt% $NH_4F$ and 8 wt% deionized water at a voltage of 60 V for 6 h. The anodization was performed in a two-electrode electrochemical cell with Ti wire (diameter of 127 μm and purity of 99.9%) and Pt sheet as anode and cathode, respectively. The modified wire was washed with deionized water two times to remove the electrolyte thoroughly, followed by heating to 500 $^o$C for 1 h and annealing in air. The modified Ti wire was then immersed into a 100 mM $TiCl_4$ aqueous solution at 70 ℃ for 30 min, followed by annealing again at 450 $^o$C for 30 min. After the temperature was cooled to 120 $^o$C, it was immersed into 0.3 mM N719 solution in a mixture solvent of tert-butanol and dehydrated acetonitrile (volume ratio of 1/1) for 16 h. Finally, a CNT fiber was wound around the dye-absorbed working electrode with a spiral pitch of 1 mm. The twisted wire was sealed in a glass capillary tube with diameter of 0.5 mm. The electrolyte was infiltrated into the cell by a capillary force prior to the characterization.

*Measurement of the conversion efficiency of the photovoltaic wire.* As generally recognized and used, the effective illumination area was calculated by multiplying the length and diameter of the working electrode in the wire cell[1-6]. The J-V characteristics were measured by covering a photomask with a slit which was a little larger than the wire cell. The experimental setup is schematically shown in Figure S16.

*Characterization.* The structures of redox couples were characterized by Varian Mercury plus 400M. CNTs were characterized by SEM (Hitachi FE-SEM S-4800 operated at 1 kV). The J-V curves of DSCs were measured by a Keithley 2400 Source Meter under illumination (100 mW/cm$^2$) of simulated AM1.5 solar light coming from a solar simulator (Oriel-Sol3A 94023A equipped with a 450 W Xe lamp and an AM1.5 filter). The light intensity was calibrated using a reference Si solar cell (Oriel-91150). The electrochemical impedance spectroscopy was performed on a CHI 660a electrochemical workstation. The cyclic voltammetry was performed in an acetonitrile solution containing 5 mM $T^-$, 0.5 mM $T_2$ and 0.1 M $LiClO_4$ with a scan rate of 50 mV s$^{-1}$ through a three-electrode setup.

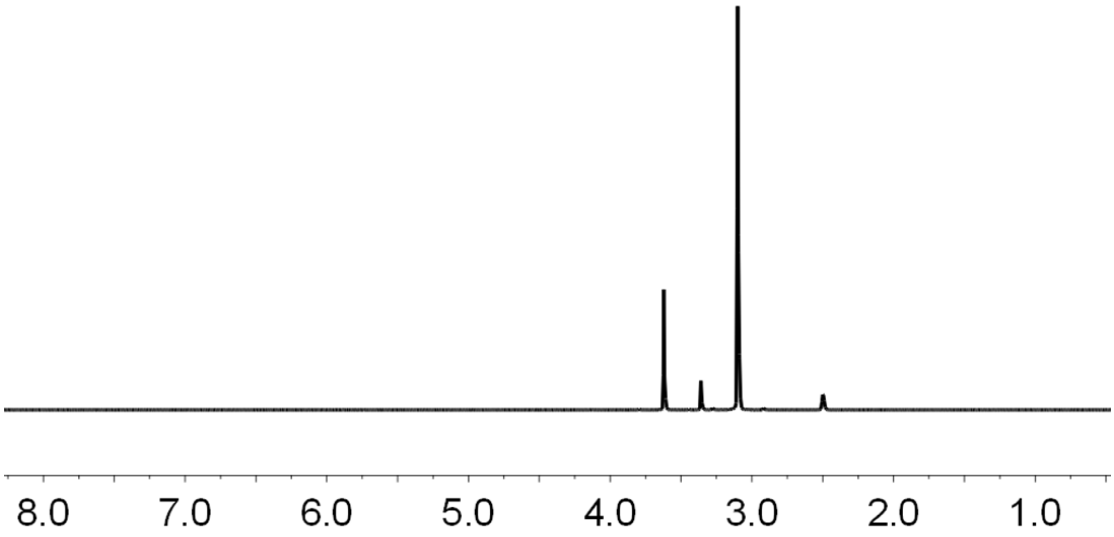


**Figure S1.** $^{1}$H NMR spectrum of $NMe_4^+T^-$ in DMSO-$d_6$.

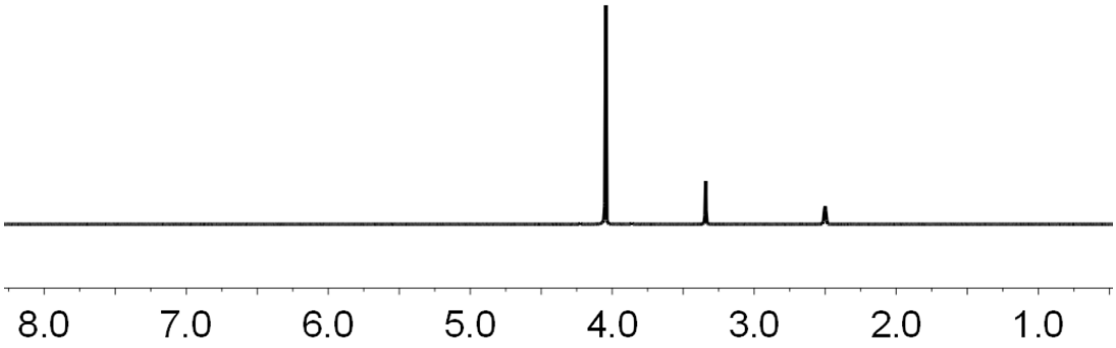


**Figure S2.** $^{1}$H NMR spectrum of $T_2$ in DMSO-$d_6$.

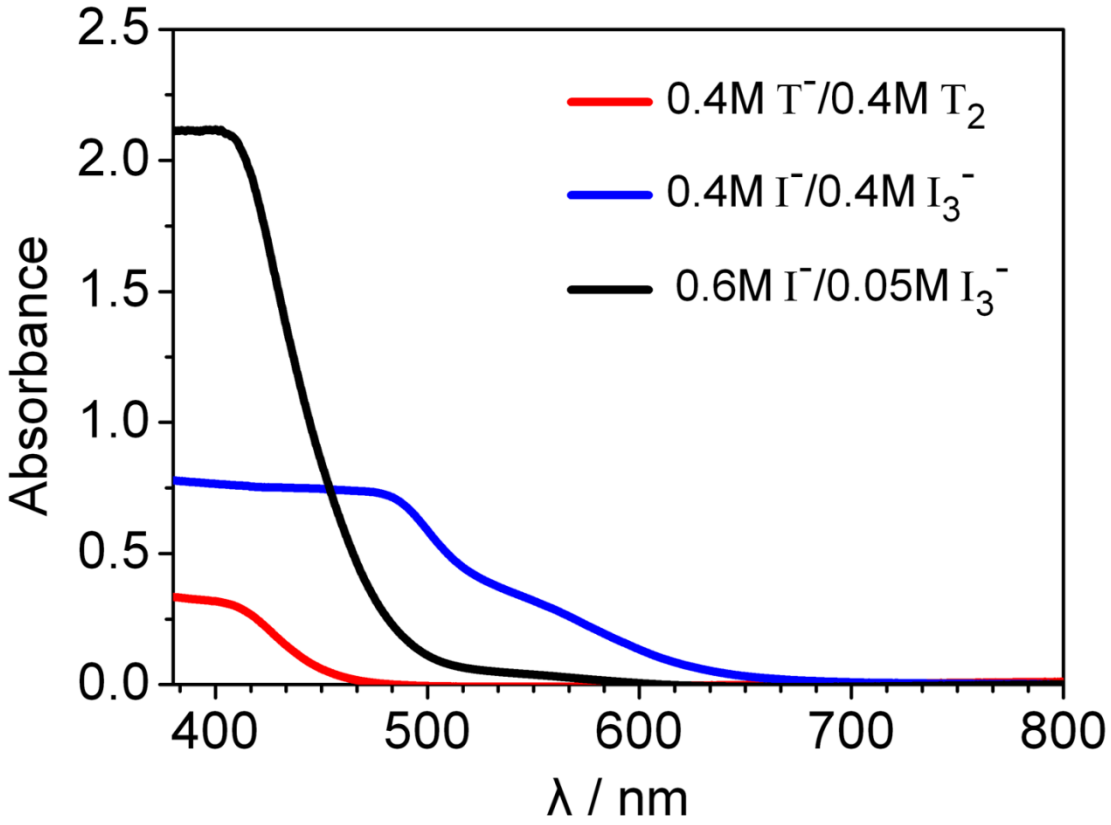


**Figure S3.** UV/Vis spectra of different electrolytes.

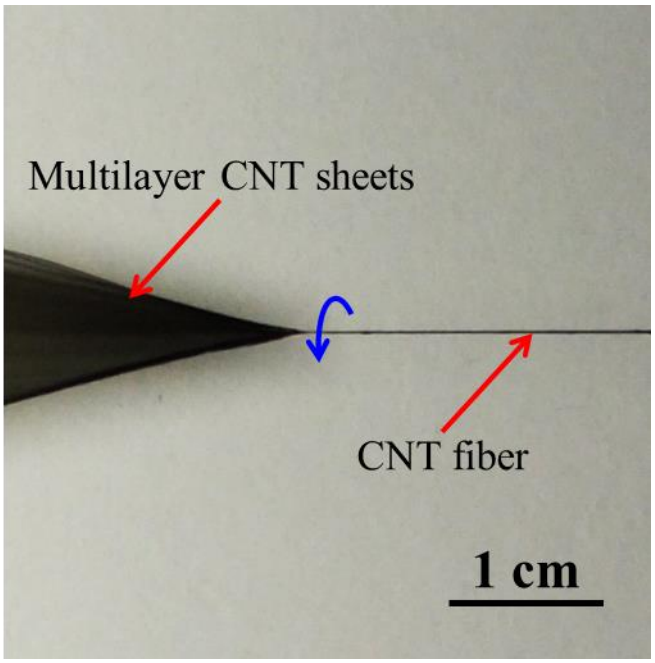


**Figure S4.** Schematic illustration to the experimental setup to prepare a CNT fiber from many layers of CNT sheets. The blue arrow shows the rotary direction.

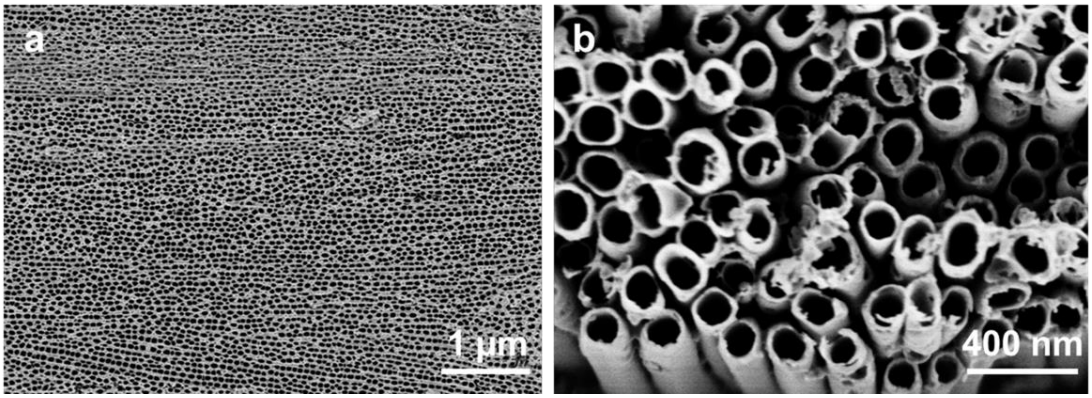


**Figure S5.** Scanning electron microscopy images of perpendicularly aligned titania nanotubes on a Ti surface. **a** and **b**. Low and high magnifications, respectively.

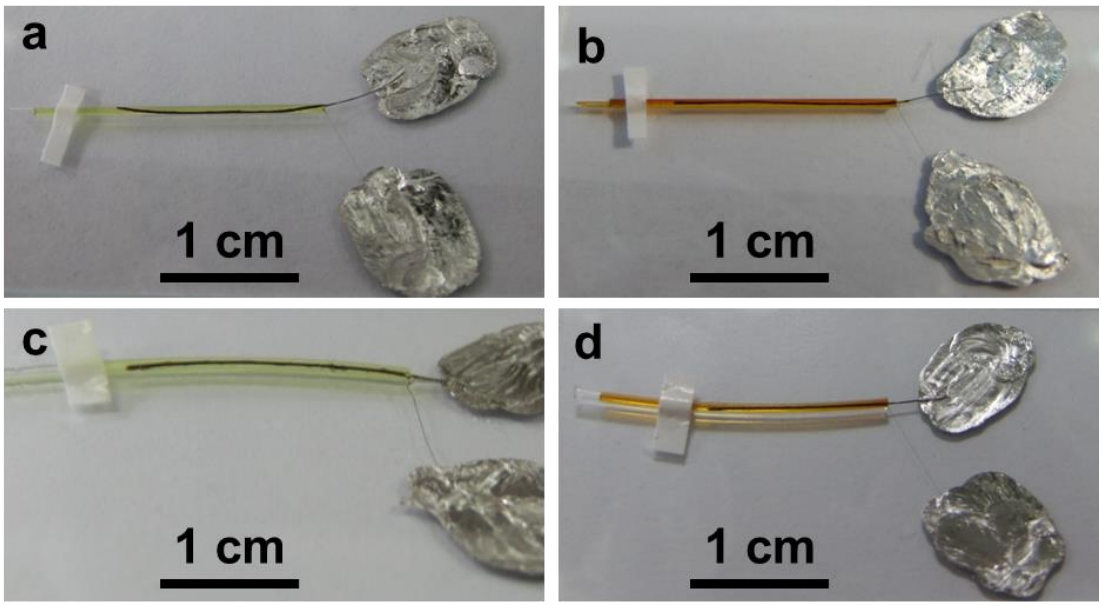


**Figure S6.** Photographs of the dye-sensitized photovoltaic wires with different electrolytes sealed in capillary glass tube and flexible (fluorinatedethylenepropylene) tubes. **a** and **c**. $T^-/T_2$ electrolyte in glass tube and (fluorinatedethylenepropylene) tubes, respectively. **b** and **d.** $I^-/I_2$ electrolyte in glass tube and (fluorinatedethylenepropylene) tubes, respectively.

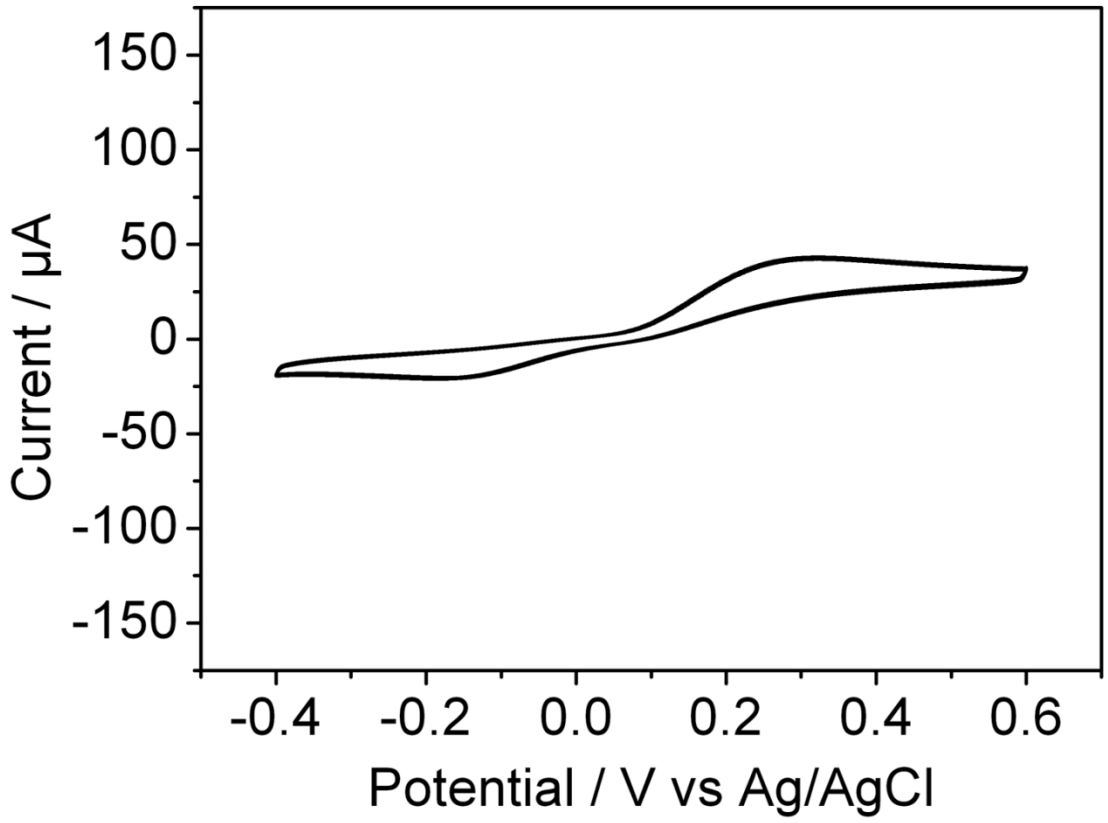


**Figure S7.** Cyclic voltammograms of a CNT fiber (diameter of 25 μm) in the $T^-/T_2$ electrolyte for ten cycles.

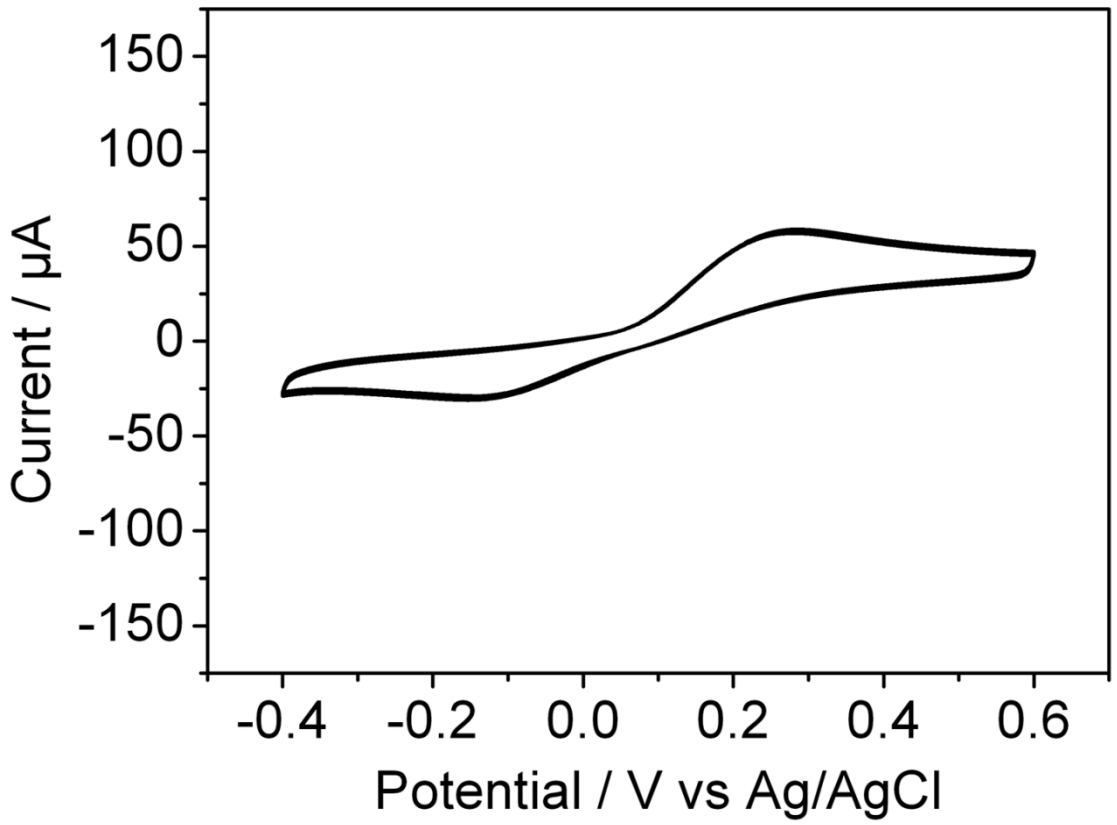


**Figure S8.** Cyclic voltammograms of a CNT fiber (diameter of 40 μm) in the $T^-/T_2$ electrolyte for ten cycles.

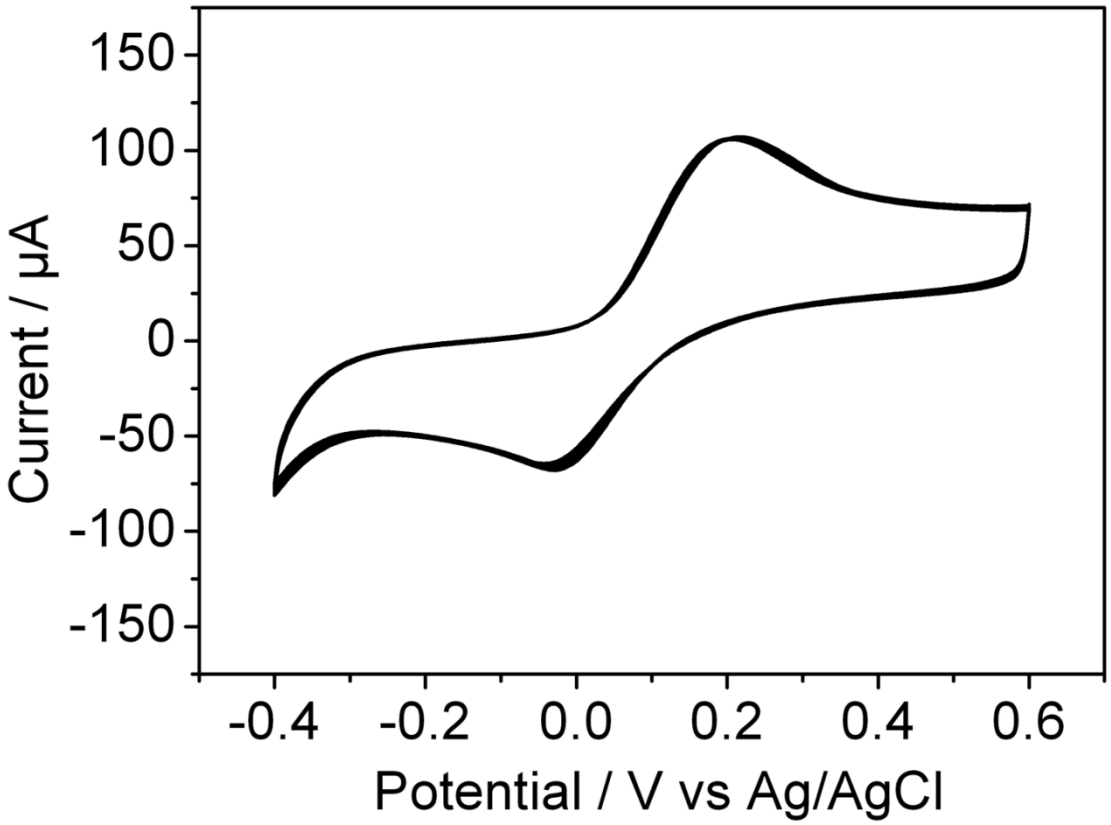


**Figure S9.** Cyclic voltammograms of a CNT fiber (diameter of 60 μm) in the $T^-/T_2$ electrolyte for ten cycles.

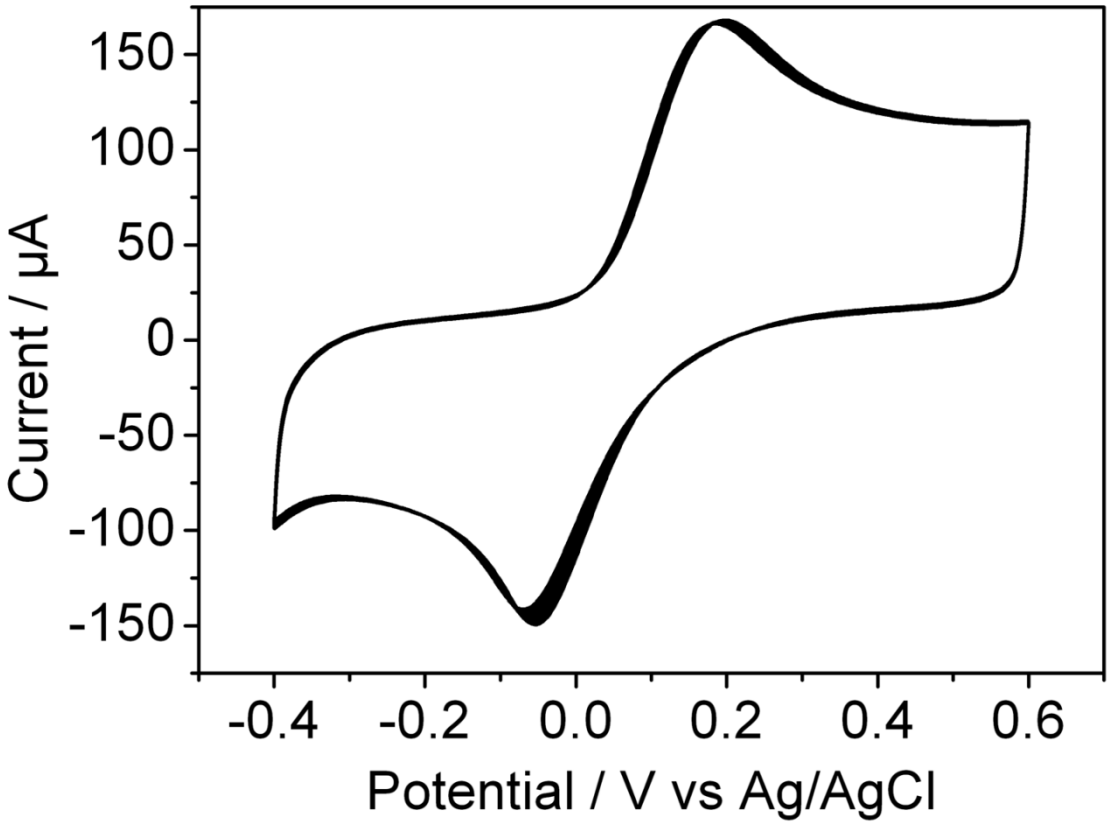


**Figure S10.** Cyclic voltammograms of a CNT fiber (diameter of 100 μm) in the $T^-/T_2$ electrolyte for ten cycles.

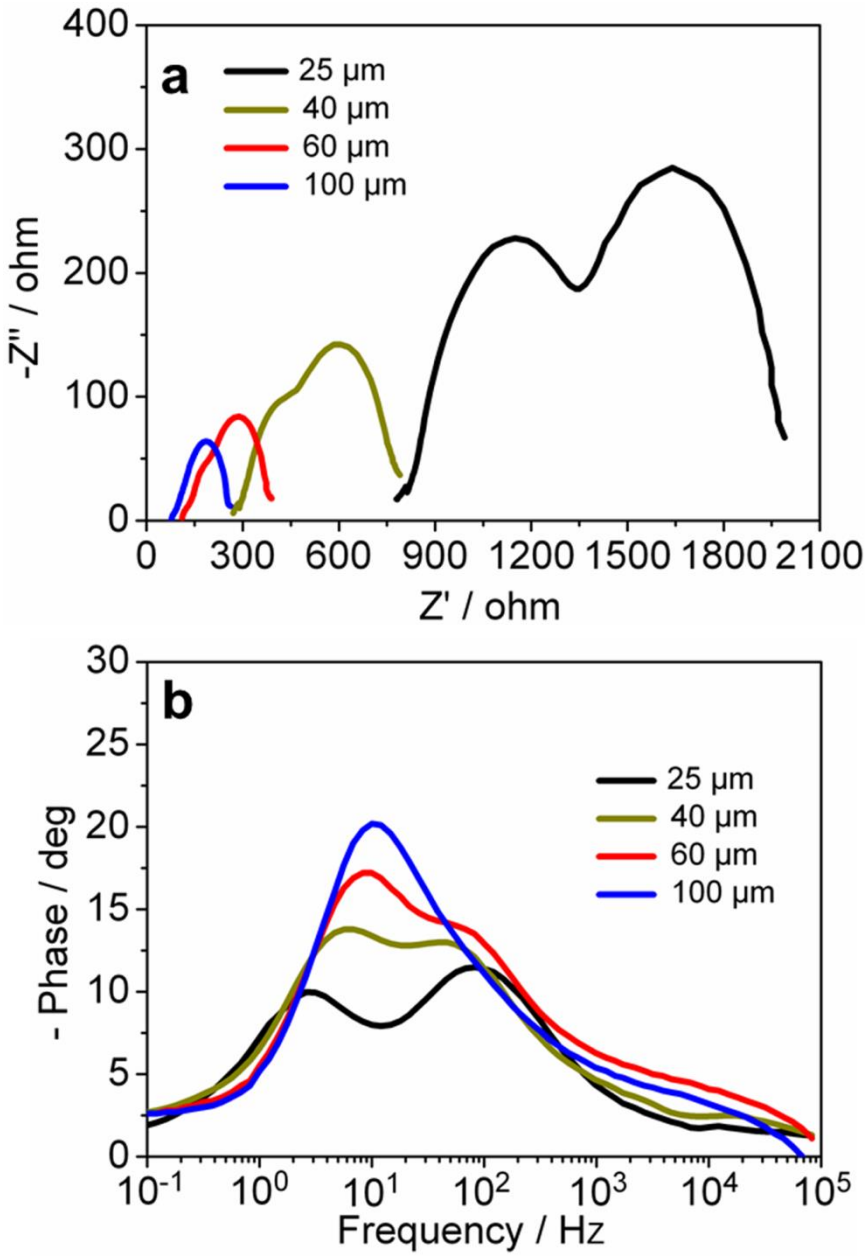


**Figure S11.** Representative Nyquist spectra of photovoltaic wires fabricated from CNT fibers with increasing diameters of 25, 40, 60 and 100 μm as counter electrodes in the $T^-/T_2$ electrolyte. The frequencies were ranged from 0.1 to 100 kHz with an applied voltage of -0.75 V in dark. **a.** Nyquist plots of photovoltaic wires. **b.** Bode plots of photovoltaic wires.

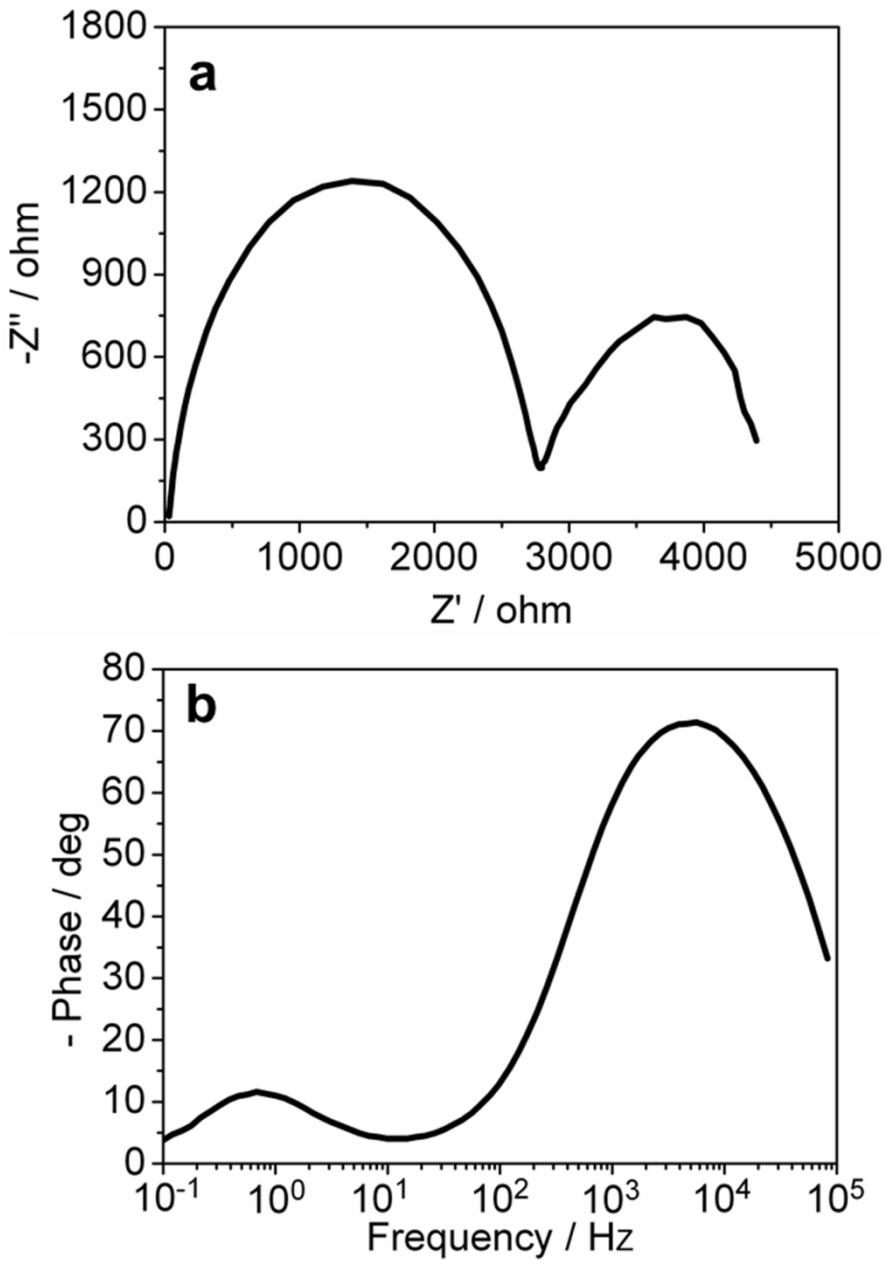


**Figure S12.** Representative Nyquist spectra of a photovoltaic wire with a Pt wire (diameter of 25 μm) as the counter electrode in the $T^-/T_2$ electrolyte. The frequencies were ranged from 0.1 to 100 kHz with an applied voltage of -0.75 V in dark. **a.** Nyquist plots of the photovoltaic wire. **b.** Bode plot of the photovoltaic wire.

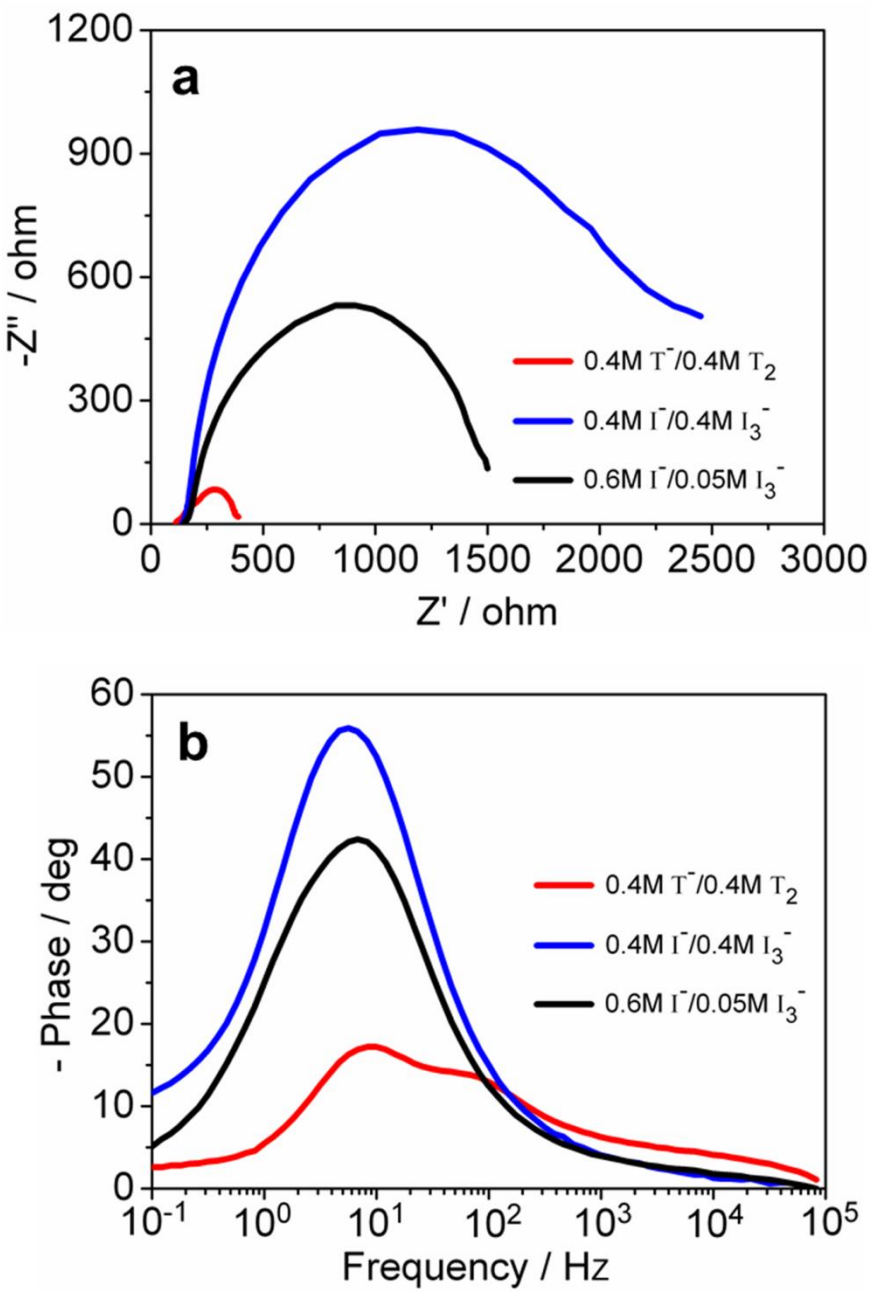


**Figure S13.** Representative Nyquist spectra of photovoltaic wires using $T^-/T_2$ and $I^-/I_3^-$ as the redox couple with the same CNT fiber (diameter of 60 μm) as the counter electrode. The frequencies were ranged from 0.1 to 100 kHz with an applied voltage of -0.75 V in dark. **a.** Nyquist plots of photovoltaic wires. **b.** Bode plots of photovoltaic wires.

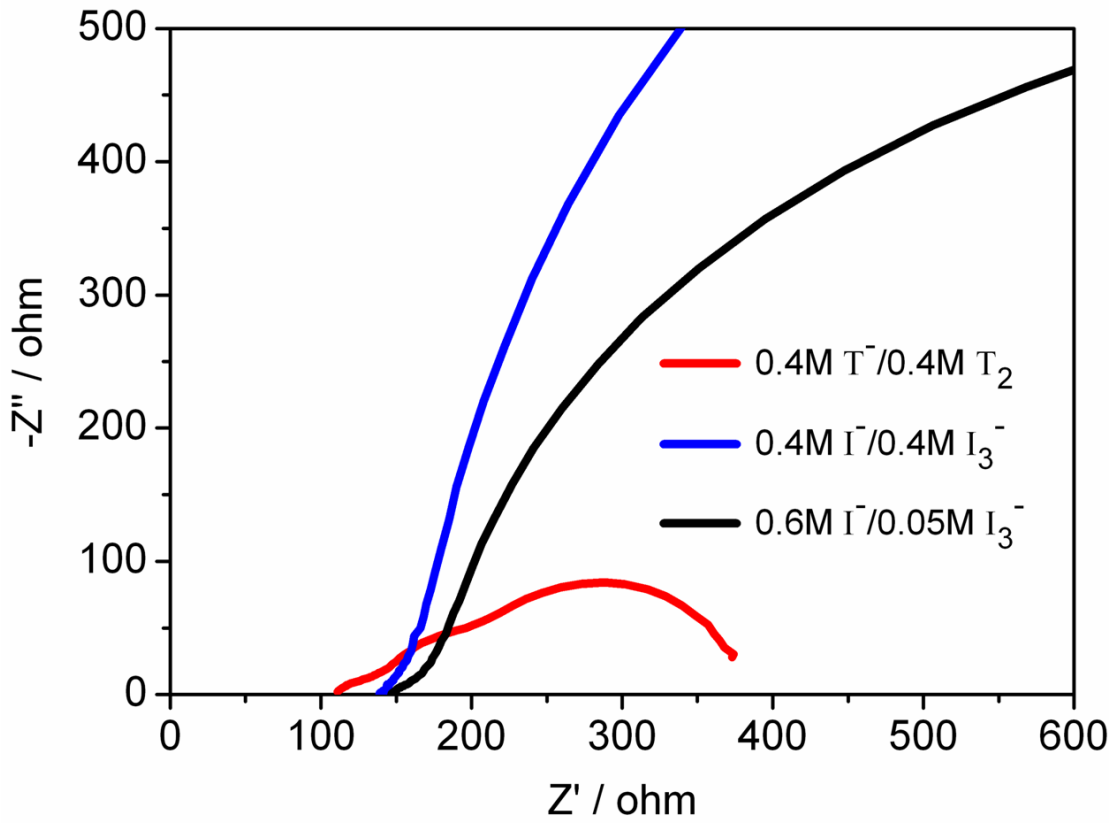


**Figure S14.** A magnified part of Figure S13a.

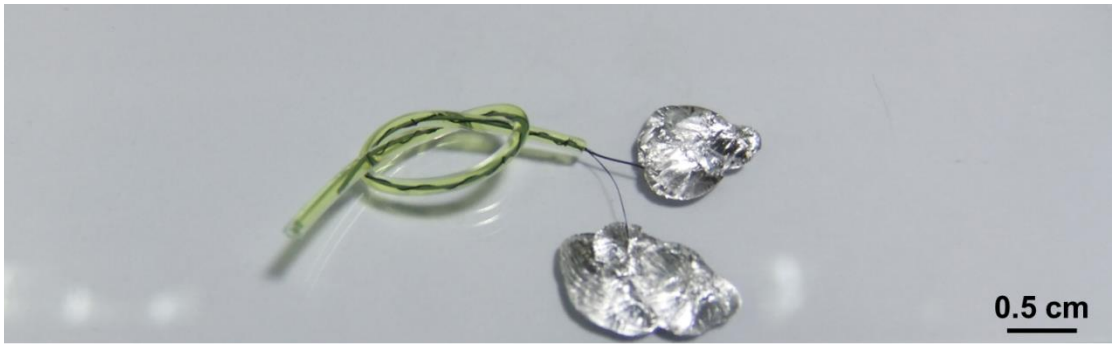


**Figure S15.** Photograph of a photovoltaic wire being made into a knot.

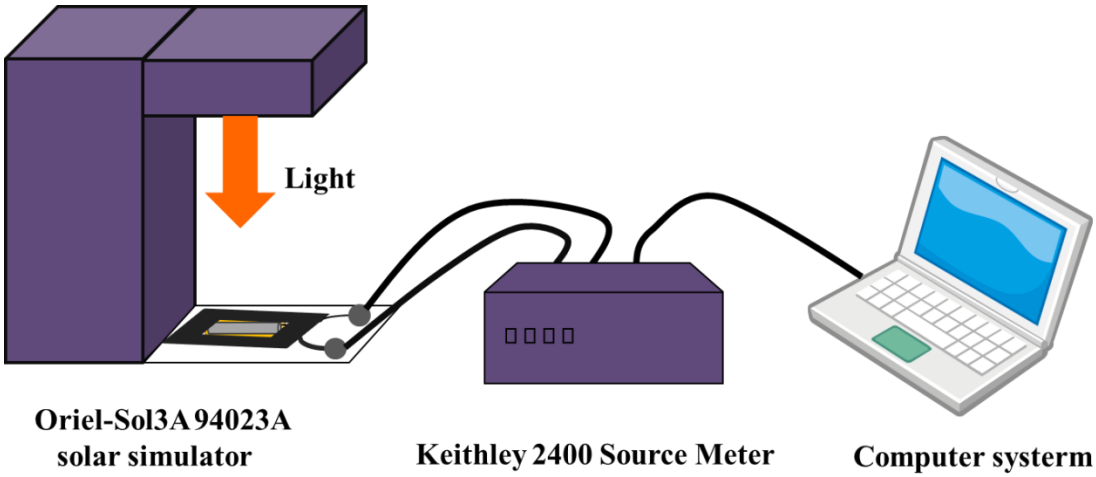


**Figure S16.** Schematic illustration to the experimental setup for the measurement of the J–V curve of the photovoltaic wire.

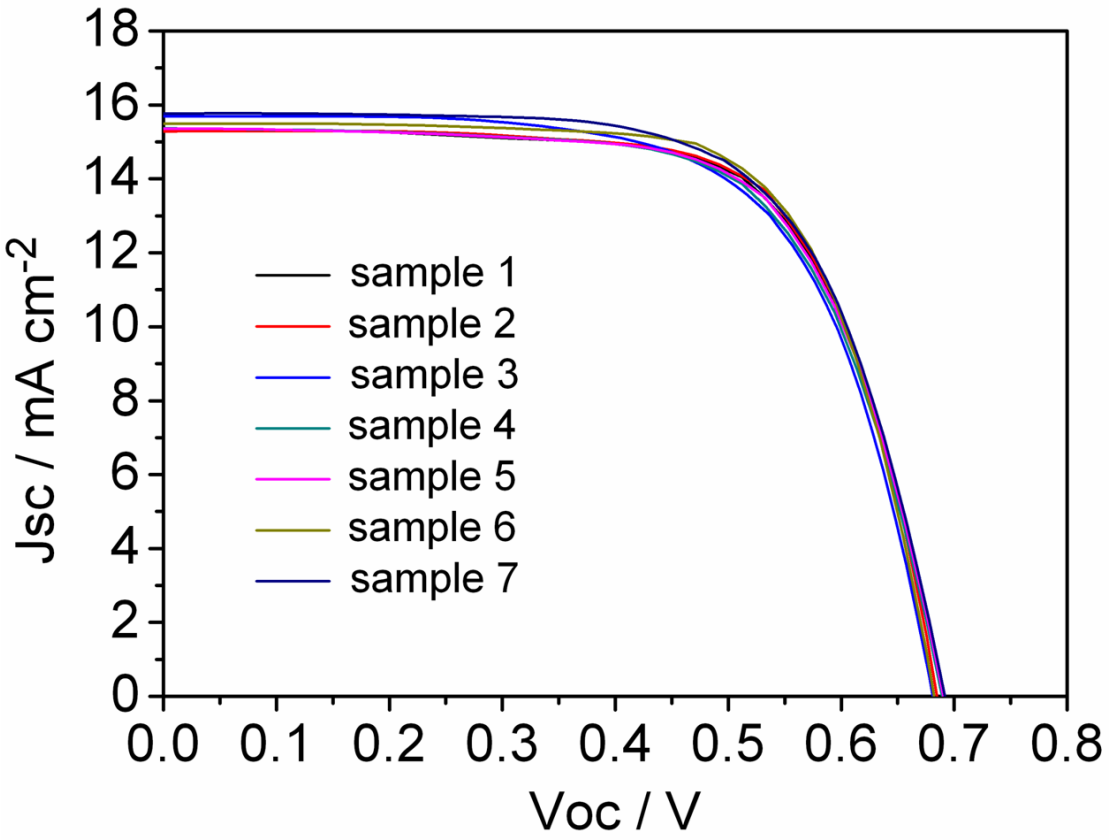


**Figure S17.** J-V curves of a series of photovoltaic wires using $T^-/T_2$ as the redox couple with the same CNT fiber (diameter of 60 μm) as the counter electrode, measured under AM 1.5 illumination. The electrolyte contains 0.4M $T^-$, 0.4M $T_2$, 0.05 M $LiClO_4$, and 0.5M 4-tert butyl-pyridine in dehydrated acetonitrile.

**Table S1.** Photovoltaic parameters in Figure S17.

| Sample | $V_{oc}$/mV | $J_{sc}$/mA $cm^{-2}$ | FF | η/(%) |
|---|---|---|---|---|
| 1 | 689 | 15.35 | 0.68 | 7.19 |
| 2 | 685 | 15.29 | 0.69 | 7.24 |
| 3 | 680 | 15.69 | 0.66 | 7.01 |
| 4 | 688 | 15.36 | 0.68 | 7.08 |
| 5 | 689 | 15.36 | 0.67 | 7.16 |
| 6 | 683 | 15.49 | 0.69 | 7.33 |
| 7 | 689 | 15.76 | 0.67 | 7.26 |

**Table S2.** Photovoltaic parameters of photovoltaic wires using $I^-/I_3^-$ as the redox couple with the same CNT fiber (diameter of 60 μm) as the counter electrode, measured under AM 1.5 illumination. The same electrolyte containing 0.5M 4-tert butyl-pyridine in dehydrated acetonitrile is used.

| Electrolyte | $V_{oc}$/mV | $J_{sc}$/mA cm$^{-2}$ | FF | η/(%) |
|---|---|---|---|---|
| 0.2M $I^-$/0.05M $I_2$ | 734 | 12.27 | 0.65 | 5.87 |
| 0.4M $I^-$/0.05M $I_2$ | 739 | 9.95 | 0.69 | 5.12 |
| 0.6M $I^-$/0.05M $I_2$ | 742 | 13.36 | 0.60 | 5.97 |
| 0.8M $I^-$/0.05M $I_2$ | 749 | 10.68 | 0.72 | 5.80 |
| 0.2M $I^-$/0.1M $I_2$ | 750 | 5.69 | 0.66 | 2.84 |
| 0.4M $I^-$/0.1M $I_2$ | 746 | 7.20 | 0.70 | 3.78 |
| 0.6M $I^-$/0.1M $I_2$ | 740 | 6.37 | 0.71 | 3.37 |
| 0.8M $I^-$/0.1M $I_2$ | 734 | 8.28 | 0.66 | 4.01 |
| 0.2M $I^-$/0.2M $I_2$ | 722 | 6.60 | 0.68 | 3.25 |
| 0.4M $I^-$/0.2M $I_2$ | 713 | 4.58 | 0.69 | 2.27 |
| 0.6M $I^-$/0.2M $I_2$ | 710 | 5.37 | 0.72 | 2.76 |
| 0.8M $I^-$/0.2M $I_2$ | 705 | 5.22 | 0.74 | 2.74 |

**References for the Supporting Information**


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