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Electronic Supplementary Information

Li@C_{60} Endohedral Fullerene as Supraatomic Dopant for C_{60} Electron-transporting Layer Promoting Efficiency in Perovskite Solar Cells

Hiroshi Ueno,[a,b,†] Il Jeon,[c,†] Haosheng Lin,[c] Abhishek Thote,[c] Takafumi Nakagawa,[c] Hiroshi Okada,[c] Seiichiro Izawa,[d,e] Masahiro Hiramoto,[d,e] Hirofumi Daiguji,[c] Shigeo Maruyama,[c,f] Yutaka Matsuo*[a,c,g]

[a] School of Chemistry, Northeast Normal University, Changchun, Jilin 130024, P. R. China

[b] Creative Interdisciplinary Research Division, The Frontier Research Institute for Interdisciplinary Sciences (FRIS), Tohoku University

[c] Department of Mechanical Engineering, School of Engineering, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan. E-mail: matsuo@photon.t.u-tokyo.ac.jp (YM)

[d] Division of Molecular Nanoscience, Research Center for Molecular Scale Nanoscience, Institute for Molecular Science

[e] SOKENDAI (The Graduate University for Advanced Studies)

[f] Energy Nano Engineering Lab., National Institute of Advanced Industrial Science and Technology (AIST)

[g] Institute of Materials Innovation, Institutes of Innovation for Future Society, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

Contents

General remarks

All reagents were commercially available and used as received without further purification unless otherwise noted. The Fermi level was measured using a Kelvin probe (Riken-Keiki, FAC-1). DLS measurements were performed on a Malvern Zetasizer Nano ZS. Photoluminescence measurements were conducted using JASCO FP-8300 Spectrofluorometer.

Synthesis of $Li@C_{60}$

$[Li^+@C_{60}]PF_6^-$ salt was purchased from Idea International Corporation. The anion-exchanged salt, $[Li^+@C_{60}]TFSI^-$ salt was prepared by the reported method.[S1] Decamethylferrocene was used as reductant after purification by sublimation. The dichloromethane solution of decamethylferrocene (3.0 μmol/mL, 2.0 mL, 6.0 μmol) was slowly added to a dichloromethane solution (2.5 mL) of $[Li^+@C_{60}]TFSI^-$ (5.0 mg, 5.0 μmol). Stirring for 15 min afforded a greenish black dispersion. The obtained solid was collected by filtration and washed with dichloromethane 3 times using ultrasonicator. After filtration, drying of the residue under vacuum at ambient temperature resulted in the isolation of the $Li@C_{60}$ as a black powder (2.9 mg, 4.0 μmol, 80%). For the detail of characterization, see ref S2.

Ref S1: H. Okada, Y. Matsuo, *Fuller. Nanotub. Carbon Nanostruct.*, 2014, **22**, 262.

Ref S2: (a) H. Okada, H. Ueno, Y. Takabayashi, T. Nakagawa, M. Vrankić, J. Arvanitidis, T. Kusamoto, K. Prassides, Y. Matsuo, *Carbon*, 2019, **153**, 467; (b) H. Ueno, S. Aoyagi, Y. Yamazaki, K. Ohkubo, N. Ikuma, H. Okada, T. Kato, Y. Matsuo, S. Fukuzumi, K. Kokubo, *Chem. Sci.*, 2016, **7**, 5770.

Fermi level measurement

ITO glass substrates were cleaned and sonicated with a detergent, distilled water, acetone, and isopropanol in an ultrasonic bath for 15 min. Next, ultraviolet/ozone (UV/O_3) for 15 min. Subsequently, C_{60} solution (20 mg mL^{-1}) and the same C_{60} solution mixed with 0.5%, 1.0%, 1.5%, or 2.0% of $Li@C_{60}$ were spin-coated on the ITO substrates at 3000 rpm for 30 s. The Fermi level of the film was measured by Kelvin prove without exposure to air. The Kelvin probe was housed in a glove box under a N_2 atmosphere (H_2O <1 ppm, O_2 <1 ppm).

Device fabrication

ITO patterned glass substrates with a size of 15 × 15 mm^2 and sheet resistance of 6 Ω $sq.^{-1}$ (Techno Print Co., Ltd.) were cleaned and sonicated with a detergent, distilled water, acetone, and isopropanol in an ultrasonic bath for 15 min. Next, ultraviolet/ozone (UV/O_3) for 15 min. Subsequently, 30 μL of PEDOT:PSS was spin-coated on ITO substrates at 3000 rpm for 30 s, followed by annealing at 105 ºC for 5 min. The perovskite precursor was prepared by mixing CH_3NH_3I (TCI), PbI_2 (TCI), and anhydrous dimethyl sulfoxide (TCI) (molar ratio 1:1:1) in anhydrous N,N-dimethylformamide (TCI) at a concentration of 50 wt%. The solution was filtered through a 0.45 μm poly(tetrafluoroethylene) filter before use. 25 μL of the perovskite precursor solution was spin-coated on the PEDOT:PSS layer at 4000 rpm for 30 s, and 0.5 mL of anhydrous diethyl ether was slowly dripped onto the substrate 10 s after the start of the spin-coating process. This was followed by annealing at 100 °C for 10 min. For the deposition of the ETL, C_{60} solution (10 mg mL^{-1}) and the same C_{60} solution mixed with 0.5%, 1.0%, 1.5%, or 2.0% of $Li@C_{60}$ were spin-coated at an rpm of 1000 for 30 s. Finally, a 70 nm-thick Au electrode was fabricated via thermal deposition at a constant evaporation rate of 0.05 nm s^{-1}.

Characterization

The $J-V$ characteristics were measured using a software-controlled source meter (Keithley 2400 Source-Meter) under dark conditions and the simulated sunlight irradiation of 1 sun (AM 1.5G; 100 mW cm^{-2}) using a solar simulator (EMS-35AAA, Ushio Spax Inc.) with a Ushio Xe short arc lamp 500. The source meter was calibrated using a silicon diode (BS-520BK, Bunkokeiki).