Supporting Information

A Dual-functional Asymmetric Squaraine-based Low Band Gap Hole Transporting Material for Efficient Perovskite Solar Cells

Sanghyun Paek[1,2], Malik Abdul Rub,[3] Hyeju Choi[2], Samia A. Kosa,[3] Khalid A. Alamry,[3] Jin Woo Cho[4], Peng Gao*[1], Jaejung Ko *[2], Abdullah M. Asiri,[3] Mohammad K. Nazeeruddin*[1],

[1]Group for Molecular Engineering of Functional Materials, Laboratory of Photonics and interfaces, Institute of Chemical Sciences and Engineering, Ecole polytechnique fédérale de Lausanne, CH-1951 Sion, Switzerland. E-mail: mdkhaja.nazeeruddin@epfl.ch; peng.gao@epfl.ch

[2] Department of New Material Chemistry, Korea University, Jochiwon, Chungnam 339-700, Korea. E-mail: jko@korea.ac.kr

[3]Center of Excellence for Advanced Materials Research (CEAMR), King Abdulaziz, University, Jeddah, Saudi Arabia.

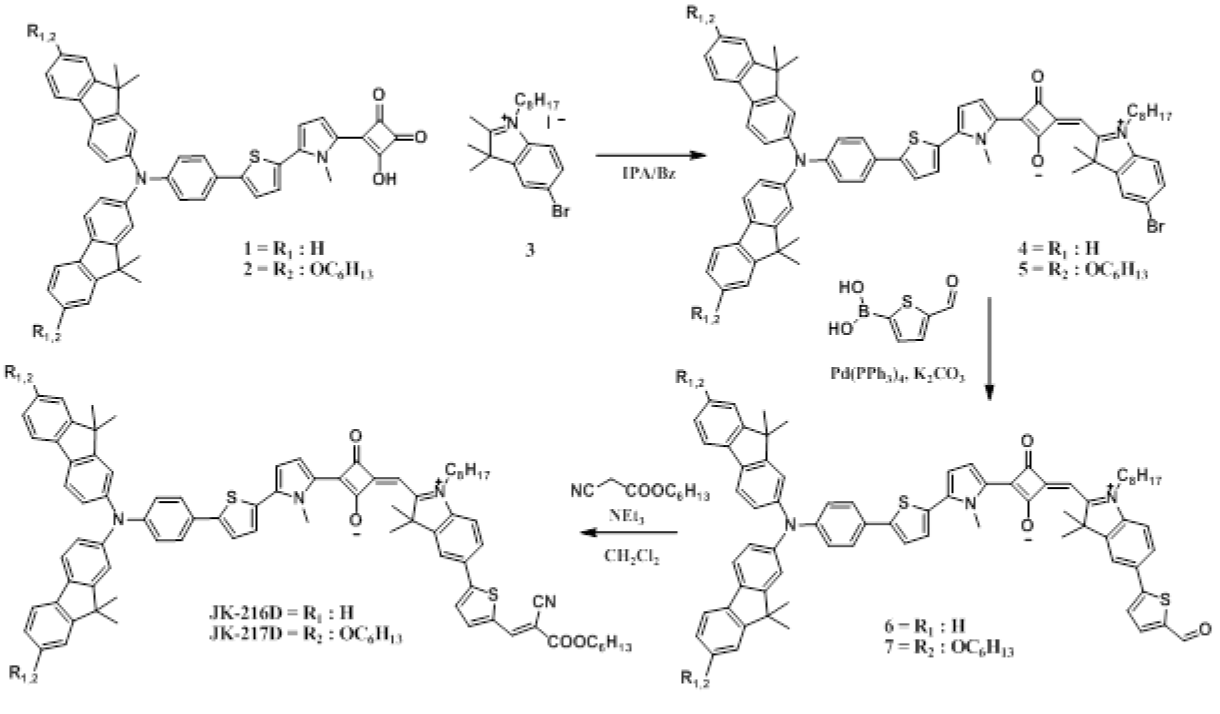
[4] LG Innotek QE team 570, Hyuanm-ro, Munsan-eup, Paju-si, Gyeongi-do 413-901, Republic of Korea

General Methods. All reactions were carried out under a nitrogen atmosphere, solvents were distilled from appropriate reagents, and all reagents were purchased from Sigma-Aldrich, TCI and Alfa Aesar.

Cyclic voltamogram. Cyclic voltammetry was carried out with a BAS 100B (Bioanalytical Systems, Inc.). A three electrode system was used and consisted of non-aqueous Reference Electrode (0.1 M Ag/Ag$^+$ acetonitrile solution; MF-2062, Bioanalytical System, Inc.), platinum working electrode (MF-2013, Bioanalytical System, Inc.), and a platinum wire (diam. 1.0 mm, 99.9 % trace metals basis, Sigma-Aldrich) as counter electrode. Redox potential of dyes was measured in CH_2Cl_2 with 0.1 M $(n\text{-}C_4H_9)_4N\text{-}PF_6$ as a scan rate of 50 mV s^{-1} (vs. Fc/Fc$^+$ as an external reference).

Measurements and Instruments. *J-V* measurements were made under simulated 100 mW/cm^2 AM 1.5G irradiation from a 1000 W Xe arc lamp (Oriel 91193). The light intensity was adjusted with a Si solar cell that was double-checked with a National Renewable Energy Laboratory (NREL)-calibrated Si solar cell (PV measurement Inc.). The applied potential and cell currents were measured using a Keithley model 2400 digital source meter. The incident photon-to-current conversion efficiency (IPCE) spectra for the cells were recorded on an IPCE measuring system (PV measurements). The film image was measured with a scanning electron microscope (SEM, FEI inc., Nova-Nano 200, Hillsboro, OR) with an acceleration voltage of 10 kV..

Experimental section



Scheme S1: Schematic diagram for the synthesis of the **JK-216D** and **JK-217D** moiety.

4. **1** (1 g, 1.3 mmol) and **3** (5-Bromo-2,3,3-trimethyl-1-octyl-3H-indolium) (0.6 g 1.3 mmol) were dissolved in a mixture of 60 ml n-propanol and 60 ml benzene. The mixture was refluxed for overnight. The solvent was removed, product **4**, was obtained by silica gel chromatography (eluent EA : Hx = 1 : 1). MS: *m/z* 1066 [M$^+$]. ^{1}H NMR(CDCl$_3$) : δ 7.72 (d, 1H, ^3J = 4.2 Hz), 7.66 (d, 2H, ^3J = 6.9 Hz), 7.62 (d, 2H, ^3J = 8.4 Hz), 7.54-7.46 (m, 4H), 7.40 (d, 2H, ^3J = 7.8 Hz), 7.35-7.26 (m, 8H), 7.20 (d, 2H, ^3J = 9.3 Hz), 7.13 (dd, 2H, ^3J = 8.4 Hz), 6.94 (d, 1H, ^3J = 8.4 Hz), 6.72 (d, 2H, ^3J = 4.2 Hz), 6.09 (s, 1H), 4.42 (s, 3H), 4.05 (t, 2H), 1.81 (m, 8H), 1.44-1.26 (m, 22H), 0.87 (t, 3H). ^{13}C{^{1}H} NMR (CDCl$_3$) : δ 184.30, 172.56, 155.31, 153.68, 148.15, 146.98, 146.21, 144.74, 141.12, 139.47, 139.00, 134.77, 131.58, 131.18, 130.59, 128.34, 127.44, 127.16, 126.75, 126.09, 123.63, 123.29, 122.65, 121.29, 120.83, 119.62, 119.10, 118.34, 115.26, 111.78, 89.30, 50.37, 47.01, 44.53, 36.28, 31.82, 29.38, 29.22, 27.40, 27.18, 27.11, 26.83, 22.70, 14.20. Anal. Calc. for $C_{68}H_{64}BrN_3O_2S$: C, 76.53; H, 6.04; N, 3.94. Found : C, 76.33; H, 6.21; N, 4.01.

5. **5** was synthesized by a procedure to **4** except that **2** (1 g, 1.07 mmol) was used in place of **1**. MS: *m/z* 1266 [M$^+$]. ^{1}H NMR(CDCl$_3$) : δ 7.72 (d, 1H, ^3J = 4.2 Hz), 7.55 (s, 1H), 7.52-7.45 (m, 7H), 7.3-7.26 (m, 2H), 7.21 (s, 2H), 7.19 (d, 2H, ^3J = 8.4 Hz), 7.08 (dd, 2H, ^3J = 8.4 Hz), 6.95-6.92 (m, 3H), 6.86 (dd, 2H, ^3J = 8.1 Hz), 6.72 (d, 1H, ^3J = 4.2 Hz), 6.08 (s, 1H), 4.42 (s, 3H), 4.01 (m, 6H), 1.81 (m, 12H), 1.49-1.26 (m, 34H), 0.94-0.85 (m, 9H). ^{13}C{^{1}H} NMR (CDCl$_3$) : δ 184.11, 172.48, 166.55, 158.96, 155.61, 154.86, 148.41, 146.42, 145.95, 144.73, 141.14, 139.57, 134.89, 131.79, 131.40, 131.17, 130.57, 128.38, 126.94, 126.68, 126.09, 123.79, 123.15, 123.08, 121.36, 120.34, 119.90, 119.27, 118.30, 115.28, 113.13, 111.77, 109.47, 89.29, 68.45, 50.36, 46.99, 44.53, 36.30, 31.83, 31.79, 29.53, 29.38, 29.22, 27.41, 27.33, 27.11, 26.83, 25.94, 22.76, 22.72, 14.20. Anal Calc. for $C_{80}H_{88}BrN_3O_4S$: C, 75.80; H, 7.00; N, 3.32. Found : C, 75.91; H, 7.03; N, 3.11.

6. Compound **4** (1 g, 0.94 mmol), 5-Formyl-2-thienylboronic acid (0.22 g, 1.45 mmol), Pd(PPh$_3$)$_4$ (75 mg, 0.06 mmol), and anhydrous K$_2$CO$_3$ (1.29 g, 4.7 mmol) were added to a

125 mL flame-dried 2-neck round-bottom flask with a condenser in THF/H_2O under a nitrogen atmosphere. The reaction mixture was heated to reflux for 14 hrs. The reaction mixture was then cooled to room temperature. The organic layer was separated and dried over anhydrous magnesium sulfate. The solvent was removed in *vacuo*. The product was purified by column chromatography (eluent EA : Hx = 1 : 1). MS: *m/z* 1097 [M^+]. ^{1}H NMR($CDCl_3$) : δ 9.90 (s, 1H), 7.75 (d, 2H, ^3J = 4.2 Hz), 7.71-7.64 (m, 6H), 7.61 (s, 1H), 7.55-7.52 (m, 3H), 7.48-7.39 (m, 5H), 7.34-7.27 (m, 4H), 7.20 (d, 2H, ^3J = 7.8 Hz), 7.15-7.11 (m, 3H), 6.74 (d, 1H, ^3J = 4.2 Hz) 6.15 (s, 1H), 4.44 (s, 3H), 4.10 (m, 2H), 1.87 (m, 8H), 1.42-1.25 (m, 22H), 0.89-0.85 (m, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) : δ 182.76, 172.44, 155.32, 153.70, 153.52, 152.34, 148.22, 146.97, 146.43, 143.81, 143.07, 142.59, 139.87, 139.00, 137.59, 134.79, 132.31, 132.19, 132.08, 131.49, 130.67, 130.17, 128.72, 128.56, 127.39, 127.18, 126.77, 124.23, 123.67, 123.59, 123.33, 122.66, 121.65, 120.83, 120.54, 119.64, 119.13, 115.45, 110.96, 90.15, 89.73, 50.19, 47.02, 44.57, 36.34, 31.84, 29.41, 29.23, 27.51, 27.19, 26.99, 22.72, 14.20. Anal. Calc. for $C_{73}H_{67}N_3O_3S_2$: C, 79.82; H, 6.15; N, 3.83. Found : C, 79.79; H, 6.21; N, 3.98.

7. **7** was synthesized by a procedure to **6** except that **5** (1 g, 0.78 mmol) was used in place of **4**. MS: *m/z* 1297 [M^+]. ^{1}H NMR($CDCl_3$) : δ 9.90 (s, 1H), 7.76 (d, 2H, ^3J = 4.2 Hz), 7.69-7.65 (m, 2H), 7.56 (s, 1H), 7.53-7.49 (m, 5H), 7.43 (d, 1H, ^3J = 4.2 Hz), 7.32 (d, 1H, ^3J = 4.2 Hz), 7.28 (d, 1H, ^3J = 4.2 Hz), 7.21 (s, 2H), 7.17 (d, 2H, ^3J = 8.1 Hz), 7.12-7.07 (m, 3H), 6.94 (s, 2H), 6.86 (dd, 2H, ^3J = 8.4 Hz), 6.74 (d, 1H, ^3J = 4.2 Hz) 6.14 (s, 1H), 4.44 (s, 3H), 4.09 (m, 2H), 4.01 (t, 4H), 1.86-1.79 (m, 12H), 1.54-1.27 (m, 34H), 0.94-0.85 (m, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) : δ 182.78, 172.34, 158.97, 155.61, 154.86, 153.55, 148.46, 146.62, 145.94, 143.80, 140.00, 137.63, 134.92, 131.79, 131.29, 130.67, 130.12, 128.55, 126.97, 126.87, 126.70, 124.24, 123.81, 123.20, 123.06, 121.75, 120.53, 120.36, 119.91, 119.29, 115.46, 113.11, 110.96, 109.47, 90.15, 89.71, 68.45, 50.17, 47.00, 44.57, 36.36, 31.86, 31.80, 29.55, 29.42, 29.25, 27.50, 27.34, 27.15, 27.01, 25.96, 22.77, 22.73, 14.22. Anal. Calc. for $C_{85}H_{91}N_3O_5S_2$: C, 78.61; H, 7.06; N, 3.24. Found : C, 78.77; H, 7.14; N, 3.29.

216D. Compound **6** (0.5 g, 0.45 mmol) and hexylcyanoacetate (1.54 g, 9.0 mmol) was dissolved in dry CH_2Cl_2 and then a few drops of triethylamine was stirred for 1 h, under nitrogen at room temperature. The solution was removed. The product was purified by column chromatography (eluent EA : Hx = 1 : 5 and then EA : MC = 1 : 1). MS: *m/z* 1247 [M^+]. ^{1}H NMR($CDCl_3$) : δ 8.30 (s, 1H), 7.77-7.75 (m, 2H), 7.72-7.61 (m, 7H), 7.54 (d, 2H, ^3J = 9.0 Hz), 7.42 (d, 1H, ^3J = 3.6 Hz), 7.42-7.18 (m, 9H), 7.20 (d, 2H, ^3J = 9.0 Hz), 7.14-7.09 (m, 3H), 6.74 (d, 1H, ^3J = 3.9 Hz) 6.15 (s, 1H), 4.44 (s, 3H), 4.31 (t, 2H), 4.10 (m, 2H), 1.87 (m, 10H), 1.42-1.25 (m, 28H), 0.89-0.85 (m, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) : δ 183.86, 172.33, 155.32, 153.80, 153.70, 148.22, 146.97, 146.50, 146.46, 143.85, 143.23, 139.95, 139.43, 139.00, 135.17, 134.79, 131.47, 130.70, 129.84, 128.53, 127.38, 127.18, 126.77, 124.50, 123.66, 123.57, 123.35, 122.66, 121.75, 120.83, 120.50, 119.64, 119.13, 116.16, 115.49, 111.00, 98.24, 89.83, 66.80, 50.20, 47.01, 36.35, 31.84, 31.52, 29.84, 29.41, 29.23, 28.65, 27.50, 27.18, 25.60, 22.72, 22.65, 14.21, 14.13. Anal. Calc. for $C_{82}H_{80}N_4O_4S_2$: C, 78.81; H, 6.45; N, 4.48. Found : C, 78.65; H, 6.61; N, 4.45.

217D. 217D was synthesized by a procedure to 21**6D** except that **7** (0.5 g, 0.38 mmol) was used in place of **6**. MS: *m/z* 1448 [M^+]. ^{1}H NMR($CDCl_3$) : δ 8.29 (s, 1H), 7.76 (m, 2H), 7.74-7.69 (m, 2H), 7.55 (s, 1H), 7.53-7.49 (m, 5H), 7.44 (d, 1H, ^3J = 4.2 Hz), 7.32 (d, 1H, ^3J = 3.3 Hz), 7.28 (d, 1H, ^3J = 3.6 Hz), 7.21 (s, 2H), 7.17 (d, 2H, ^3J = 9.0 Hz), 7.11-7.08 (m, 3H), 6.93 (s, 2H), 6.86 (dd, 2H, ^3J = 8.4 Hz), 6.74 (d, 1H, ^3J = 4.2 Hz) 6.14 (s, 1H), 4.44 (s, 3H), 4.30 (t, 2H), 4.09 (m, 2H), 4.01 (t, 4H), 1.86-1.79 (m, 14H), 1.54-1.27 (m, 40H), 0.94-0.85 (m, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) : δ 183.72, 172.23, 167.11, 163.15, 158.96, 155.61, 154.86, 153.84, 148.46, 146.65, 146.51, 145.92, 143.84, 143.26, 140.08, 139.45, 135.16, 134.92, 131.79, 131.28, 130.69, 129.79, 128.56, 127.18, 126.86, 126.70, 124.49, 123.81, 123.20, 123.04, 121.81, 120.49, 120.36, 119.90, 119.28, 116.18, 115.49, 113.11, 110.96, 109.46, 98.21, 89.79, 68.45, 66.80, 50.18, 47.00, 44.57, 36.36, 31.84, 31.79, 31.52, 29.84, 29.53, 29.41, 29.24, 28.66, 27.50, 27.33, 27.14, 27.02, 25.94, 25.61, 22.77, 22.72, 22.65, 14.20, 14.15. Anal. Calc. for $C_{94}H_{104}N_4O_6S_2$: C, 77.86; H, 7.23; N, 3.86. Found : C, 77.83; H, 7.18; N, 3.92.

Reference

1. Etgar, L.; Gao, P.; Xue, Z.; Peng, Q.; Chandiran, A. K.; Liu, B.; Nazeeruddin, Md. K.; Grätzel M. *J. Am. Chem. Soc.* **2012**, *134*, 17396−17399

2. Jeon, N. J.; Lee, H. G.; Kim,Y. C.; Seo, J.; Noh, J. H.; Lee, J.; Seok, S. I. J. Am. Che,. Soc., **2014**, 136, 7873-7840.

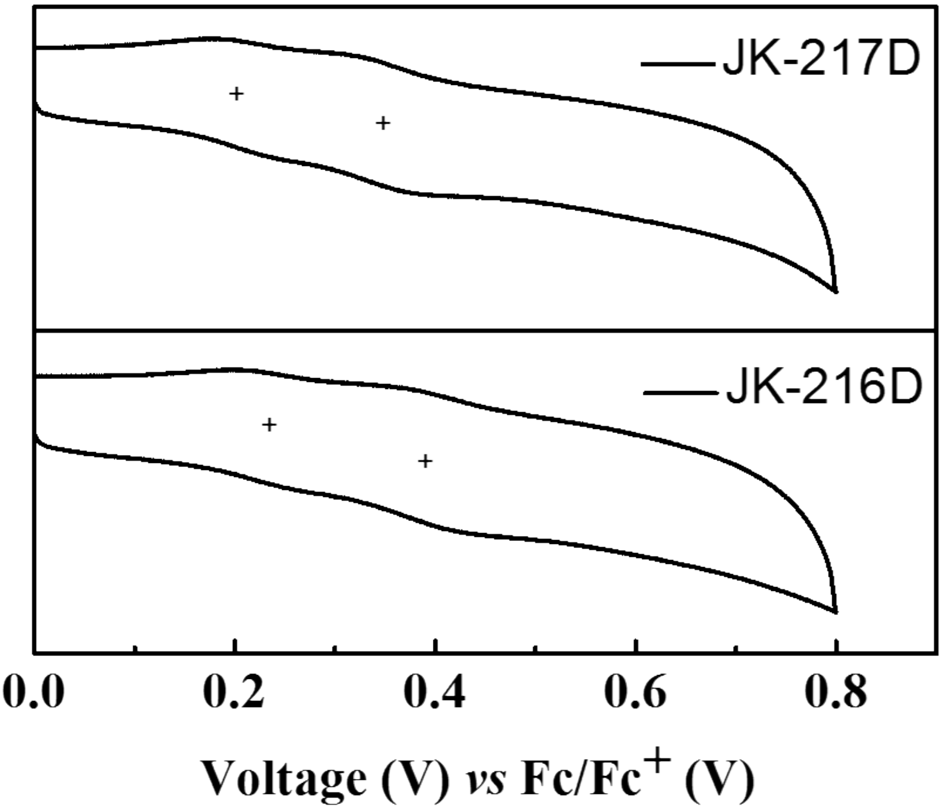


Figure S1. Electrochemical characterization (oxidation) of JK216D and JK217D in 0.1 M tetrabutyl ammonium hexafluorophosphate in CH_2Cl_2 at a scan speed of 50 mV s^{-1}, potentials vs. Fc/Fc^+.

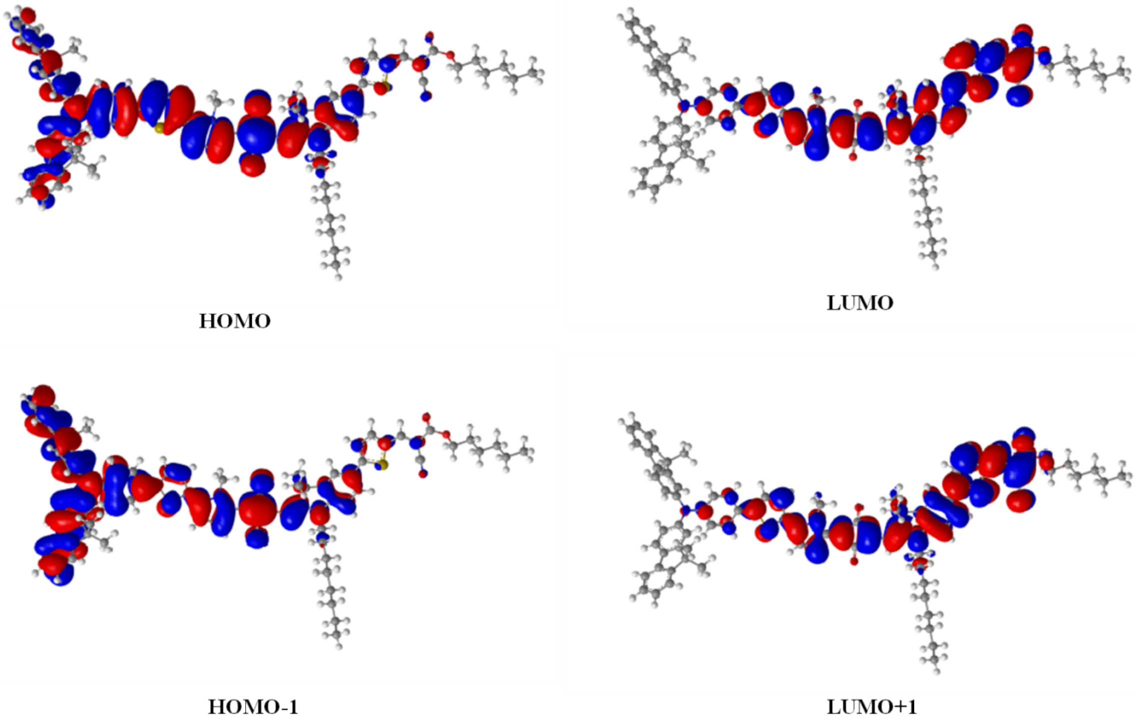


Figure S2. Isodensity surface plots of **JK-216D** calculated by the time dependent-density functional theory (TD-DFT) using the B3LYP functional/6-31G* basis set.

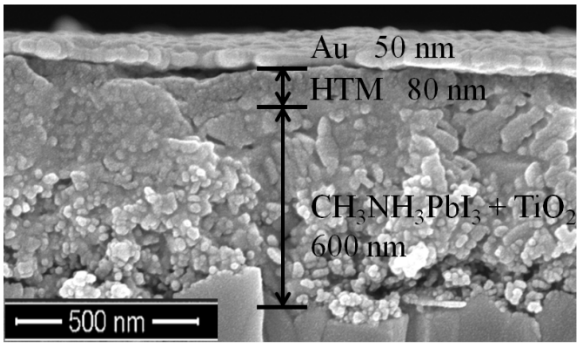


Figure S3. Cross-sectional SEM images of the CH3NH3PbI3/HTM hybrid photovoltaic cells with JK-216D as HTM layer.

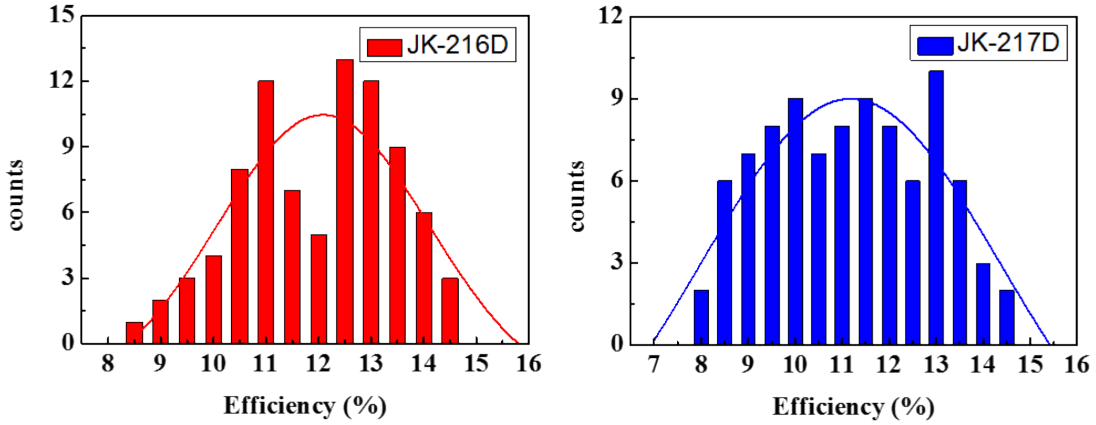


Figure S4. Histogram of the solar cell efficiencies obtained from the **JK-216D** (red line) and **JK-217D** (blue line) based hybrid solar cells.