

Supporting Information

Self-Assembled Amphiphilic Diketopyrrolopyrrole-Based Oligothiophenes for Field-Effect Transistors and Solar Cells

Jianguo Mei, Kenneth R. Graham, Romain Stalder, Shree Prakash Tiwari, Hyeunseok Cheun, Jaewon Shim, Masafumi Yoshio, Colin Nuckolls, Bernard Kippelen, Ronald K. Castellano, John R. Reynolds*

Table of Contents

1. Figure S1 Differential scanning calorimetry thermograms -----	S2
2. Figure S2 Snapshots of the directed growth of a DPP_{amphi} plastic phase -----	S2
3. Figure S3 Polarized light microscopy images of DPP_{amphi} -----	S3
4. Figure S4. Diffraction patterns obtained from DPP_{amphi} at 170, 80, and 50 °C. -----	S3
5. Figure S5 Cyclic voltammetry and differential pulse voltammetry of DPP_{amphi} ----	S3
6. Table S1 Summary of OFET devices -----	S4
7. Figure S6 <i>J-V</i> characteristics and external quantum efficiencies of a representative DPP_{amphi} : PC ₆₁ BM photovoltaic device before and after annealing -----	S4
8. S7 Synthetic details and analytical data -----	S5
9. S8 OFET fabrication details -----	S7
10. S9 Solar cell fabrication -----	S8

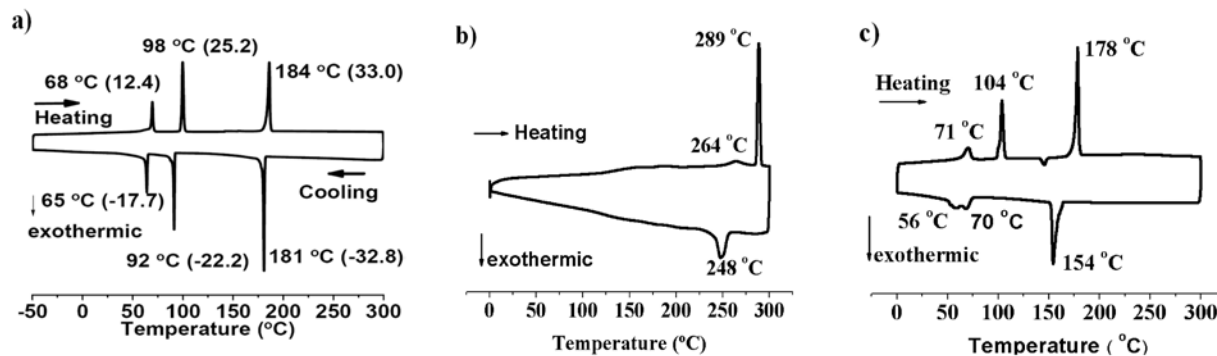


Figure S1. Differential scanning calorimetry thermograms. a) **DPP_{ampi}**, b) **PC₆₁BM**, and c) **DPP_{ampi}** and **PC₆₁BM** mixture (1:1, wt %).

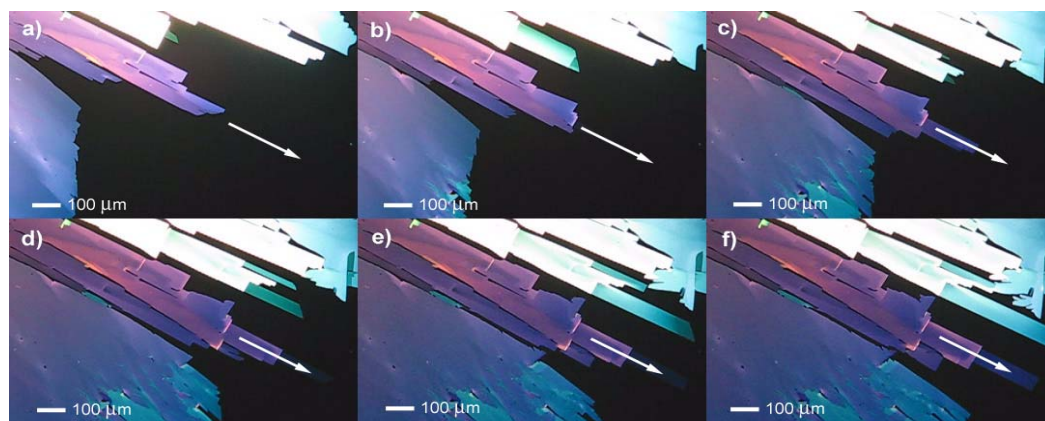


Figure S2. Snapshots of the directed growth of a **DPP_{ampi}** plastic phase as viewed by polarized light microscopy at 170 °C after shearing (pictures taken at 5 s intervals and the arrow indicates the shearing direction).

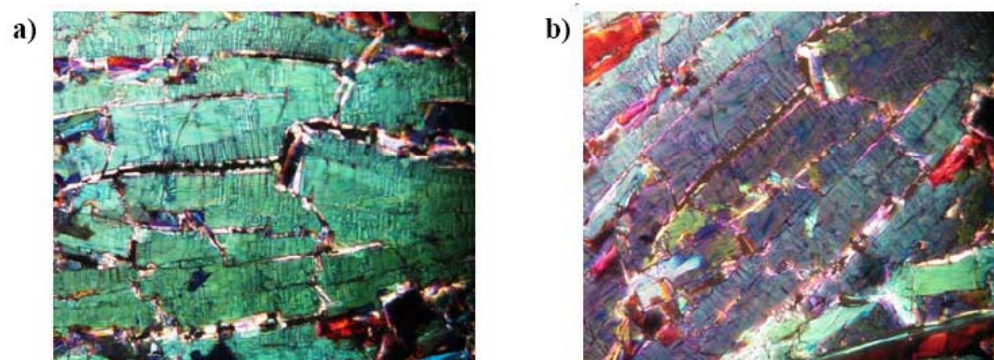


Figure S3. Polarized light microscopy images of **DPP_{ampi}** at a) 80 °C and b) RT.

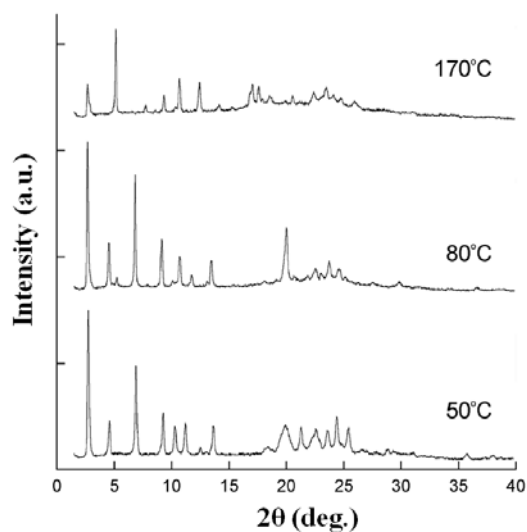


Figure S4. Diffraction patterns obtained from **DPP_{amphi}** at 170, 80, and 50 °C.

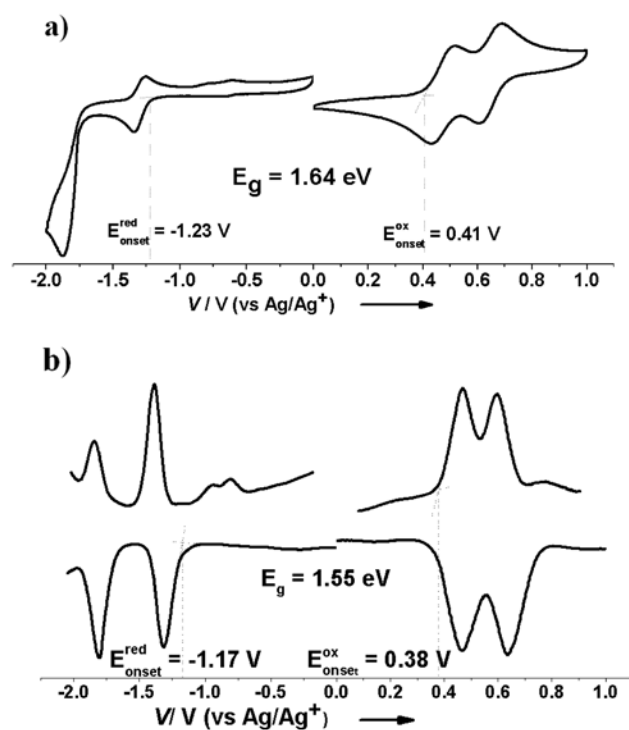


Figure S5 Cyclic voltammetry a), and differential pulse voltammetry b), of **DPP_{amphi}**.

Cyclic voltammetry (CV) of **DPP_{amphi}** in anhydrous CH_2Cl_2 showed four quasireversible consecutive redox processes with half-wave potentials around 0.65, 0.47, -1.30 and -1.79 V vs Ag/Ag^+ , respectively. The differential pulse voltammograms (DPV) for **DPP_{amphi}** revealed four

well-defined and highly reversible anodic and cathodic processes with a high degree of symmetry; the half-wave potentials are very close to the potentials observed in CV. The potential difference between the first oxidation and reduction peak of 1.77 V is in excellent agreement with the optical gap (1.77 eV) of the molecularly dissolved **DPP_{amphi}** in CH₂Cl₂ with the onset of absorption around 700 nm. Energy gaps of 1.64 eV and 1.55 eV are obtained from the differences of oxidation and reduction onset in CV and DPV. These values are close to the optical energy gap (1.55 eV) in solid state, where the absorption onset is around 850 nm.

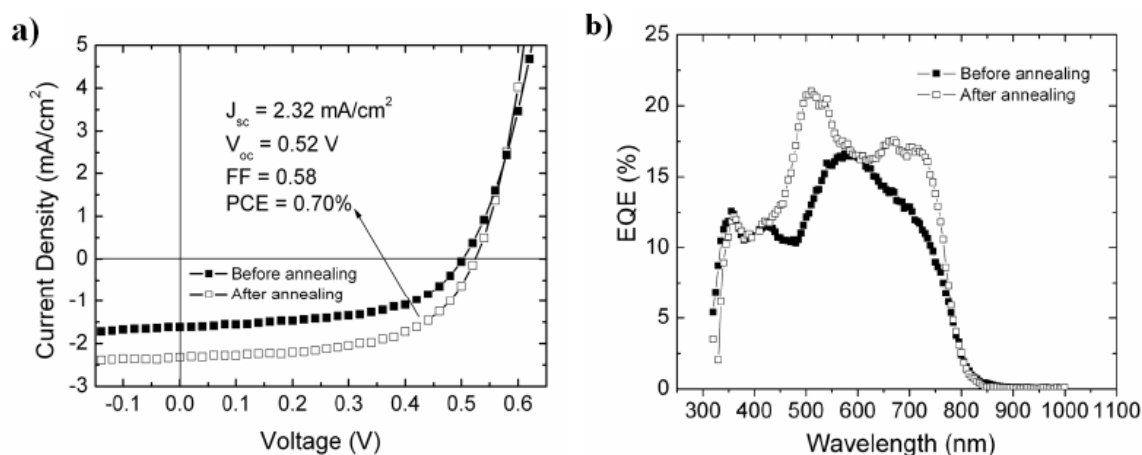
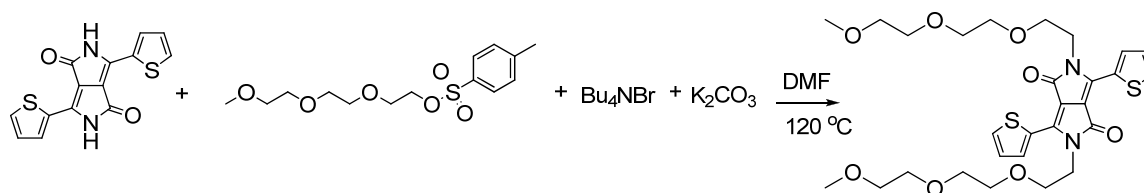


Figure S6. a) J - V characteristics and b) external quantum efficiencies of a representative **DPP_{amphi}** : PC₆₁BM photovoltaic device before and after annealing at 90 °C.

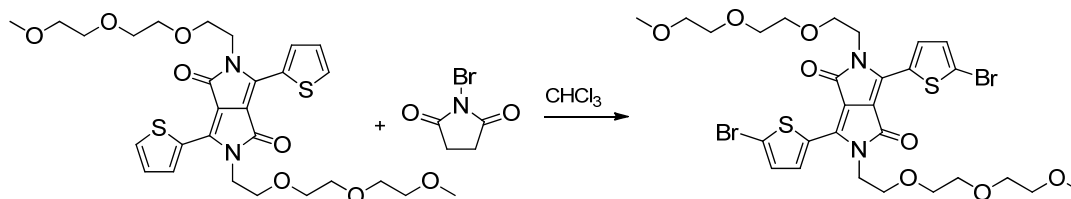
Table S1. Summary of OFET devices

W/L	μ (cm ² /Vs)	V_{TH} (V)	$I_{on/off}$
1200 μ m/25 μ m (3 Dev.)	4.1 ($\pm$ 0.4) $\times 10^{-3}$	6.3 ($\pm$ 0.1)	1 $\times 10^4$
1200 μ m/50 μ m (4 Dev.)	3.2 ($\pm$ 0.8) $\times 10^{-3}$	2.5 ($\pm$ 1.3)	8 $\times 10^3$
1200 μ m/100 μ m (4 Dev.)	3.0 ($\pm$ 0.3) $\times 10^{-3}$	1.5 ($\pm$ 0.4)	3 $\times 10^3$

S7. Synthetic details and analytical data

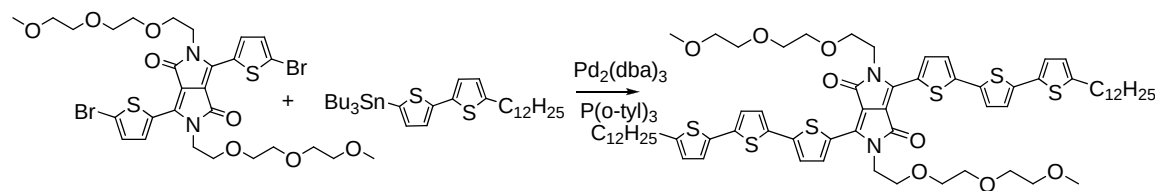


***N,N'*-Bis-(10-(3,6,9-trioxadecyl)-3,6-di(5-thienyl)-1,4-diketo-pyrrolo[3,4-c]pyrrole.** To a mixture of 3,6-bis-(2-thienyl)-1,4-dioxopyrrolo[3,4-c]pyrrole (4.5 g, 15 mmol), tetrabutylammonium bromide (0.5 g, 1.5 mmol) and potassium carbonate (10.4 g, 75 mmol) in DMF (120 mL), 2-(2-(2-methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate (18.1 g, 57 mmol) in DMF (30 mL) was added. The mixture was heated up to 120 °C and stirred for 40 h. DMF was removed under vacuum. To the concentrated solution, distilled water (150 mL) was added. The organic phases were extracted with CHCl₃ (5 × 50 mL), washed with brine, and dried over MgSO₄. Viscous purple liquids obtained were purified by silica gel chromatography, eluting with CH₂Cl₂ / acetone (9:1 to 8:2) to give red solids (4.1 g, 46%). ¹H-NMR (CDCl₃) δ: 8.69 (dd, *J*₁ = 1.2 Hz, *J*₂ = 3.9 Hz, 2H), 7.56 (dd, *J*₁ = 1.2 Hz, *J*₂ = 5.1 Hz, 2H), 7.17 (dd, *J*₁ = 3.9 Hz, *J*₂ = 5.1 Hz, 2H), 4.19 (t, *J* = 6.3 Hz, 4H), 3.71 (t, *J* = 6 Hz, 2H), 3.59–3.39 (m, 16H), 3.26 (s, 6H) ppm. ¹³C-NMR (CDCl₃) δ: 161.6, 140.5, 135.0, 131.1, 129.9, 128.6, 108.0, 72.1, 70.9, 70.7, 69.1, 59.2, 42.0 ppm. HRMS (ESI-TOF) calculated for C₂₈H₃₆N₂O₈S₂ (M+H)⁺: 593.1986, found: *m/z* 593.1982. Anal. calcd for C₂₈H₃₆N₂O₈S₂: C, 56.74; H, 6.12; N, 4.73; found: C, 55.88; H, 6.12; N, 4.67.



***N,N'*-Bis-(10-(3,6,9-trioxadecyl)-3,6-di(5-bromothieryl)-1,4-diketo-pyrrolo[3,4-*c*]pyrrole.**

To a solution of *N,N'*-bis-(10-(3,6,9-trioxadecyl)-3,6-di(5-thienyl)-1,4-diketo-pyrrolo[3,4-*c*]pyrrole (593 mg, 1.0 mmol) in CHCl₃ (50 mL), *N*-bromosuccinimide (NBS) (374 mg, 2.1 mmol) was added in one portion. The solution was stirred for 48 h at rt in the dark (covered with aluminum foil). After the reaction was complete (indicated by TLC), distilled water was added. The organic phases were washed by brine and dried over MgSO₄. Dark purple solids obtained were purified by silica gel chromatography, eluting with CH₂Cl₂/ acetone (9:1) to give violet-purple solids (456 mg, 61%). ¹H-NMR (CDCl₃) δ: 8.46 (d, *J* = 4.5 Hz, 2H), 7.16 (d, *J* = 4.5 Hz, 2H), 4.12 (t, *J* = 6.0 Hz, 4H), 3.73 (t, *J* = 6.0 Hz, 4H), 3.61–3.43 (m, 16H), 3.10 (s, 6H) ppm. ¹³C-NMR (CDCl₃) δ: 161.3, 139.6, 135.0, 131.5, 131.3, 119.4, 108.1, 72.1, 70.9, 70.7, 69.1, 59.1, 42.4 ppm. HRMS (ESI-TOF) calculated for C₂₈H₃₄Br₂N₂O₈S₂ (M+H)⁺: 751.0183, found: *m/z* 751.0161. Anal. calcd for C₂₈H₃₄Br₂N₂O₈S₂: C, 44.81; H, 4.57; N, 3.73; found: C, 44.51; H, 5.53; N, 3.71.

***N,N'*-Bis-(10-(3,6,9-trioxadecyl)-3,6-di(5''-dodecyl-terthienyl)-1,4-diketo-pyrrolo[3,4-*c*]pyrrole.**

To a Schlenk flask (125 mL) charged with a stirring bar were added *N,N'*-bis-(10-(3,6,9-trioxadecyl)-3,6-di(5-bromothieryl)-1,4-diketo-pyrrolo[3,4-*c*]pyrrole (750 mg, 1 mmol), tributyl(5'-dodecyl-2,2'-bithiophen-5-yl)stannane (1560 mg, 2.50 mmol), Pd₂(dba)₃ (20 mg) and P(*o*-tyl)₃ (24 mg). The mixture was purged with argon gas followed by application of vacuum for 10 min. The process was repeated three times and the flask was refilled with argon. Degassed toluene (20 mL) was injected through a septum. The resulting mixture was heated up to 80 °C

under argon and stirred for 20 h. The reaction mixture was poured into hexane and the precipitates were collected by vacuum filtration. Dark olive-green solids were further purified by silica gel chromatography, eluting with CHCl_3 / acetone (from 96:4 to 92:8) to give purple solids (708 mg, 49%). $^1\text{H-NMR}$ (CDCl_3) δ : 8.78 (d, $J = 4.2$ Hz, 2H), 7.20 (d, $J = 4.2$ Hz, 2H), 7.18 (d, $J = 3.9$ Hz, 2H), 7.00 (d, $J = 3.9$ Hz, 2H), 6.99 (d, $J = 3.6$ Hz, 2H), 6.67 (d, $J = 3.6$ Hz, 2H), 4.27 (t, $J = 6.0$ Hz, 4H), 3.82 (t, $J = 6.0$ Hz, 4H), 3.67–3.44 (m, 16H), 3.31 (s, 6H), 2.80 (t, $J = 7.5$ Hz, 4H), 1.70 (quintet, 4H), 1.40–1.20 (m, 36H), 0.90 (t, $J = 7.2$ Hz, 6H) ppm. $^{13}\text{C-NMR}$ (CDCl_3) δ : 161.4, 146.6, 143.0, 139.2, 136.5, 134.2, 128.1, 126.2, 125.2, 124.6, 124.2, 124.0, 108.4, 72.1, 71.0, 70.8, 69.2, 59.2, 42.2, 32.1, 31.8, 30.4, 29.88, 29.85, 29.8, 29.59, 29.57, 29.3, 22.9, 14.3 ppm. HRMS (ESI-TOF) calculated for $\text{C}_{68}\text{H}_{92}\text{N}_2\text{O}_8\text{S}_6$ ($\text{M}+\text{Na}$) $^+$: 1279.5070, found: m/z 1279.5065. Anal. calcd for $\text{C}_{68}\text{H}_{92}\text{N}_2\text{O}_8\text{S}_6$: C, 64.93; H, 7.37; N, 2.23; found: C, 64.81; H, 7.35; N, 2.23.

S8. Field-effect transistor fabrication

OFETs were fabricated on heavily doped n-type silicon substrates (also serving as gate electrodes) with 200 nm thick thermally grown SiO_2 as the gate dielectric, in a top contact configuration. Ti/Au (10 nm/100 nm) metallization on the backside of the substrate was done to enhance the gate electrical contact. First, the substrates were cleaned by O_2 plasma for three minutes, to ensure the proper film formation by changing the surface character of SiO_2 to hydrophilic. The capacitance density (C_{OX}) was measured from 12 parallel-plate capacitors of varying area, and yielded a value of ~ 16.2 nF/cm ^{2} . A thin layer of organic semiconductor was formed on the substrates by spin coating with a 10 mg/mL solution of **DPP_{amphi}** in chlorobenzene. A ~ 75 nm-thick Au layer was deposited through a shadow mask to act as top source/drain electrode. The device fabrication was performed under inert (N_2) atmosphere. The

samples were transferred in a vacuum tight vessel, without being exposed to atmospheric conditions, into a N₂-filled glovebox (O₂, H₂O ~ 0.1 ppm) for electrical testing. The devices were then thermally annealed at 130 °C for 30 minutes before device characterization.

S9 Solar cell fabrication

The fabrication of a **DPP_{amphi}** : PC₆₁BM based solar cell device is described below. ITO-coated glass (Colorado Concept Coating LLC), with a resistivity of ~15Ω/sq, served as both the anode electrode and the substrate. The ITO/glass substrate was rinsed with acetone and wiped with nonwoven tissues to remove glass-particles still adhering from the cutting step. Next, the substrate was cleaned by immersion in deionized water with detergent in an ultrasonic bath for 10 min at 60 °C. Afterwards, the substrate was rinsed with plenty of deionized water and ultrasonic cleaning with deionized water was performed for 10 minutes at 60 °C. The substrate was again rinsed with plenty of deionized water. The substrate was next cleaned in sequential ultrasonic baths of ethanol and deionized water for 5 minutes each. A final ultrasonic cleaning in acetone for 5 minutes at 40 °C was then done. After each bath, the substrate was dried with nitrogen. Next, SiO_x(300nm) was deposited on the cleaned ITO surface by electron beam deposition (AXXIS, Kurt J. Lesker) at a rate of 50 nm/s under a pressure of 3.3×10^{-7} Torr at rt. Prior to deposition of the hole conducting layer, the ITO/glass substrate with SiO_x was cleaned with isopropanol by ultrasonication for 10 min, and the surface was prepared by exposure to air plasma for 3 min. PEDOT:PSS (CLEVIOS P VP AI 4083 PE FL), a hole conductor, was filtered through 0.45μm-pore-PVDF filters and spin-coated on the substrate at a speed of 5000 rpm for 1 min followed by annealing at 140 °C for 10 min in atmosphere. The next fabrication step involved the solution-based deposition of the active layer. **DPP_{amphi}**:PC₆₁BM (Nano-C) (7:3 by

weight) was dissolved in chloroform for a concentration of 20 mg/ml without any filtration. The solution was then filtered through a 0.45 μ m-PTFE filter and spin-coated on top of the PEDOT:PSS layer at 1500 rpm for 1 minute. Deposition of the **DPP**_{amphi}:PC₆₁BM film was performed in an M-Braun nitrogen glove box.

The substrate was loaded on a shadow mask defining cathodes and loaded into a thermal evaporation system (SPECTROS, Kurt J. Lesker) connected to the glove box. Al electrodes (200 nm) were deposited on the top of the active layer at a rate of 0.1–0.2 nm/s under a pressure of 2.2×10^{-7} Torr at rt. Electrical properties were measured with a source meter (2400 Keithley) controlled by a LabVIEW program in a nitrogen environment. For testing the solar cell properties under illumination, an AM1.5 G solar simulator (Oriel, 91160) with an irradiance $I_L = 108.8 \text{ mW/cm}^2$ was used in the glovebox as a broad light source.