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Electronic Supporting Information

Synthesis, properties, and photovoltaic characteristics of p-type donor copolymers having fluorine-substituted benzodioxocyclohexene-annelated thiophene

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Supplementary Figures and Tables

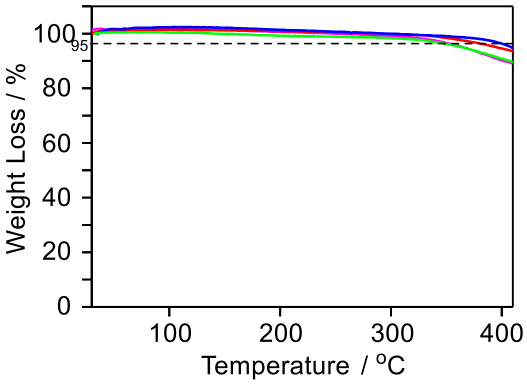


Fig. S1 TGA curves of **DTS-C_0** (purple), **DTS-C_0(F_2)** (red), **DTS-C_0(F_4)** (green), and **DTS-C_6(F_2)** (blue) with a scanning rate of 10 °C min^{-1} under N_2.

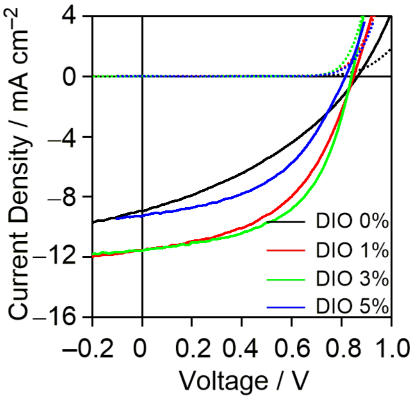


Fig. S2 J–V curves of the **DTS-C_0(F_2)**:$PC_{71}BM$ OPV devices for the optimization of DIO.

Table S1 Optimization of DIO for **DTS-C_0(F)$_2$**:$PC_{71}BM$ blend films.

DIO /wt%	V_{OC} /V	J_{SC} /mA cm^{-2}	FF	PCE /%
0	0.86	8.93	0.36	2.76
1.0	0.85	11.53	0.49	4.80
3.0	0.84	11.58	0.54	5.28
5.0	0.82	10.13	0.46	3.81

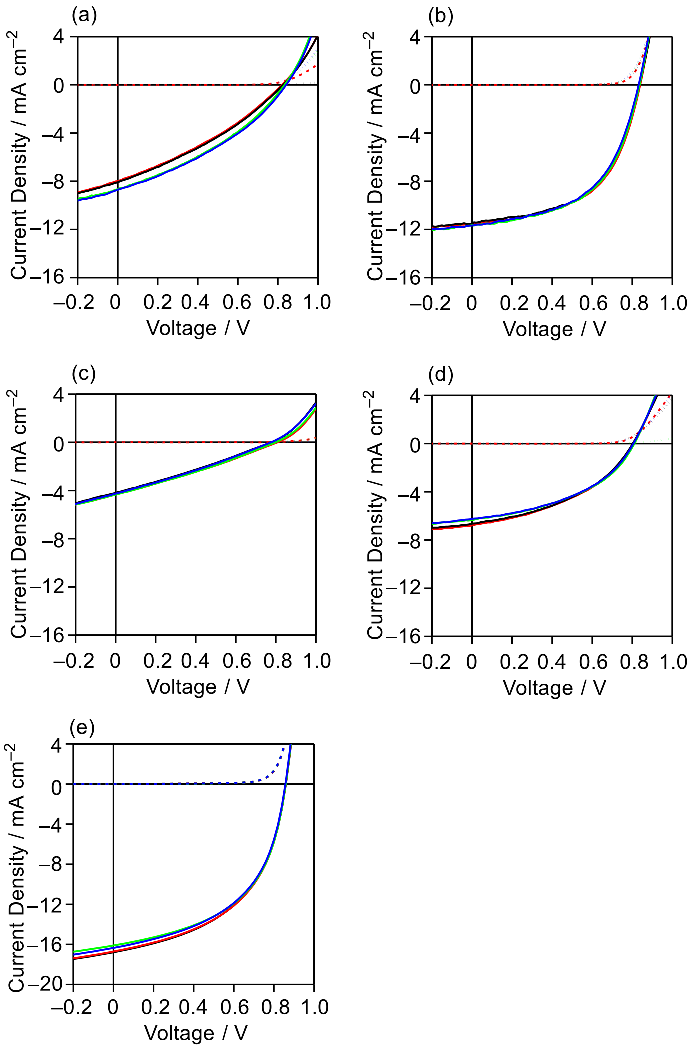


Fig. S3 *J*–*V* curves of the (a) **DTS-C$_0$**:PC$_{71}$BM, (b) **DTS-C$_0$(F$_2$)**:PC$_{71}$BM, (c) **DTS-C$_0$(F$_4$)**:PC$_{71}$BM, (d) **DTS-C$_6$(F$_2$)**:PC$_{71}$BM, and (e) optimized **DTS-C$_0$(F$_2$)**:PC$_{71}$BM OPV devices.

Table S2 OPV performance based on **DTS-C$_0$**:PC$_{71}$BM blend films.

run	V_{OC} /V	J_{SC} /mA cm^{-2}	FF	PCE /%
1	0.84	8.72	0.35	2.55
2	0.83	8.66	0.35	2.51
3	0.83	8.10	0.32	2.17
4	0.82	8.00	0.32	2.11
average	0.83 ± 0.01	8.37 ± 0.32	0.34 ± 0.02	2.34 ± 0.20

Table S3 OPV performance based on **DTS-C_0(F_2)**:$PC_{71}BM$ blend films.

run	V_{OC} /V	J_{SC} /mA cm^{-2}	FF	PCE /%
1	0.84	11.58	0.54	5.28
2	0.84	11.52	0.54	5.16
3	0.83	11.68	0.53	5.15
4	0.84	11.64	0.54	5.23
average	0.84 ± 0.00	11.61 ± 0.06	0.54 ± 0.00	5.21 ± 0.05

Table S4 OPV performance based on **DTS-C_0(F_4)**:$PC_{71}BM$ blend films.

run	V_{OC} /V	J_{SC} /mA cm^{-2}	FF	PCE /%
1	0.81	4.32	0.28	0.99
2	0.78	4.19	0.28	0.91
3	0.80	4.34	0.28	0.99
4	0.78	4.26	0.28	0.93
average	0.79 ± 0.01	4.28 ± 0.06	0.28 ± 0.00	0.96 ± 0.04

Table S5 OPV performance based on **DTS-C_6(F_2)**:$PC_{71}BM$ blend films.

run	V_{OC} /V	J_{SC} /mA cm^{-2}	FF	PCE /%
1	0.81	6.79	0.41	2.26
2	0.80	6.64	0.42	2.23
3	0.81	6.35	0.43	2.21
4	0.81	6.25	0.43	2.19
average	0.81 ± 0.00	6.51 ± 0.22	0.42 ± 0.01	2.22 ± 0.03

Table S6 Optimized OPV performance based on **DTS-C_0(F_2)**:$PC_{71}BM$ blend films.

run	V_{OC} /V	J_{SC} /mA cm^{-2}	FF	PCE /%
1	0.86	16.79	0.50	7.28
2	0.86	16.71	0.51	7.30
3	0.86	16.11	0.52	7.19
4	0.86	16.35	0.51	7.14
average	0.86 ± 0.00	16.49 ± 0.27	0.51 ± 0.01	7.23 ± 0.07

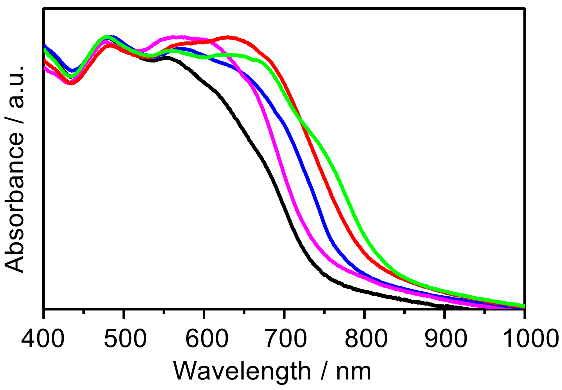


Fig. S4 UV-vis spectra of **DTS-C_0**:$PC_{71}BM$ (purple), **DTS-$C_0(F_2)$**:$PC_{71}BM$ (red), **DTS-$C_0(F_4)$**:$PC_{71}BM$ (green), **DTS-$C_6(F_2)$**:$PC_{71}BM$ (blue), and reference polymer **DTS-C_6**:$PC_{71}BM$ (black) films.

Table S7 Photophysical properties of copolymer and blend films

Compounds	$\lambda_{onset}^{copolymer}$ /nm [a)]	λ_{onset}^{blend} /nm [a)]	Δ [b)]
DTS-C_0	755	761	6
DTS-$C_0(F_2)$	779	826	47
DTS-$C_0(F_4)$	816	832	16
DTS-$C_6(F_2)$	751	785	34
DTS-C_6	738	747	9

a) In film. b) $\Delta = \lambda_{onset}^{blend} - \lambda_{onset}^{copolymer}$

Table S8 Summary of SFE for copolymers

Compounds	γ_d / mJ cm^{-2}	γ_p / mJ cm^{-2}	SFE / mJ cm^{-2}
DTS-C_0	18.2	3.6	21.8
DTS-$C_0(F_2)$	19.7	4.1	21.8
DTS-$C_0(F_4)$	14.1	4.5	18.6
DTS-$C_6(F_2)$	15.2	3.3	18.5
DTS-C_6	18.5	2.8	20.3

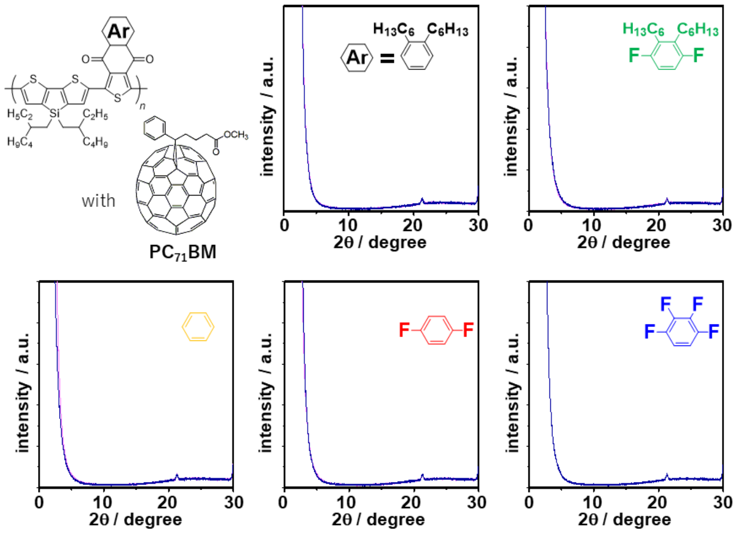


Fig. S5 XRD of blend films.

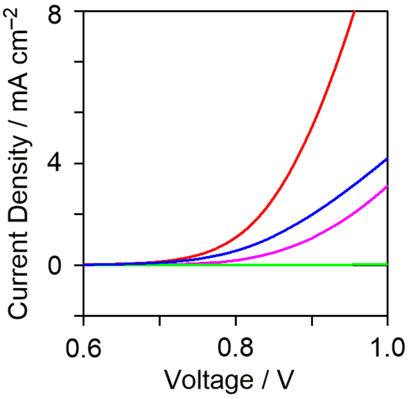


Fig. S6 Magnified *J*–*V* characteristics in the dark condition for **DTS-C$_0$**:PC$_{71}$BM (pink), **DTS-C$_0$(F$_2$)**:PC$_{71}$BM (red), **DTS-C$_0$(F$_4$)**:PC$_{71}$BM (green), and **DTS-C$_6$(F$_2$)**:PC$_{71}$BM (blue) films.

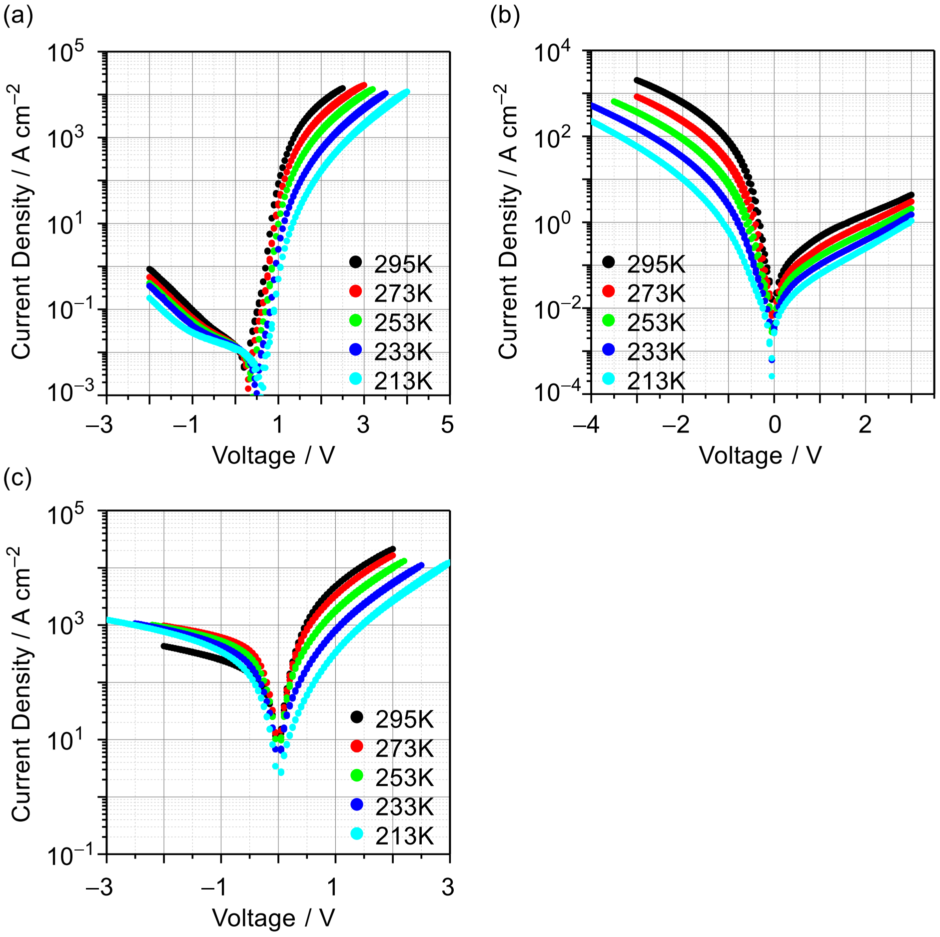


Fig. S7 J–V characteristics of (a) double-carrier (b) hole-only, and (c) electron-only devices for **DTS-C$_0$(F$_2$)**:PC$_{71}$BM films.

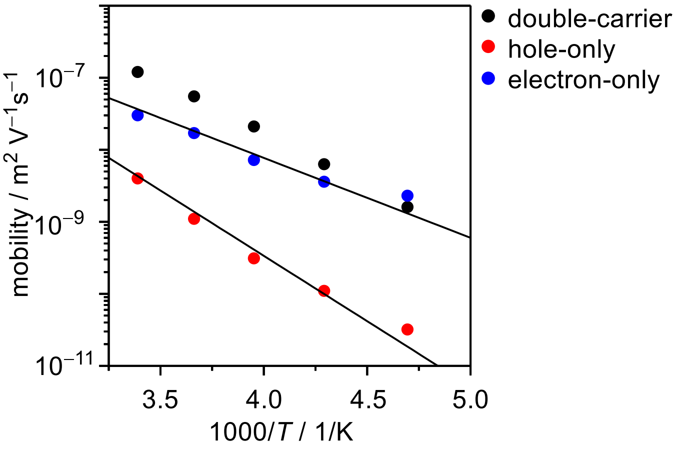


Fig. S8 Temperature dependence of carrier mobility for **DTS-C$_0$F$_2$**/PC$_{71}$BM films. Black solid lines were fitted from the equation $\mu = \mu_0 \exp(-E_a/kT)$, where E_a is an activation energy, k is Boltzmann's constant, and μ_0 is the mobility at $1000/T = 0$.

Experimental Procedures

General Information. TGA was performed under nitrogen at a heating rate of 10 °C min^{-1} with a Shimadzu a Shimadzu TGA-50. UV-vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer. PESA was carried out using a Riken Keiki Co. Ltd. AC-3 with a light intensity of 20 mW. All spectra were obtained in spectrograde solvents. The surface structures of the deposited organic films were observed by atomic force microscopy (Shimadzu, SPM9600).

General Information of Synthesis. Column chromatography was performed on silica gel, KANTO Chemical silica gel 60N (40–50 μm). Thin-layer chromatography plates were visualized with UV light. Microwave irradiation was performed by a Biotage Initiator Ver. 2.5. The microwave power output was set at 400 W. The reaction temperature was kept at 180 ºC, and internal temperature during the reaction was monitored by IR sensor. Analytical GPC was performed on a Hitachi High-Technologies Corporation L-2420/L-2130 equipped with a Shodex K-803L at 40 ºC using chloroform ($CHCl_3$) as an eluent. Preparative GPC was performed on a Japan Analytical Industry LC-918 equipped with JAI-GEL 1H/2H. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECS-400 spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), coupling constant (Hz). Mass spectra were obtained on a Shimadzu GCMS-QP-5050. High-resolution mass spectrum (HRMS) was obtained atmospheric pressure chemical ionization (APCI) method using a Thermo scientific LTQ Orbitrap XL. Elemental analysis was performed on Perkin Elmer LS-50B by the Elemental Analysis Section of CAC, ISIR, Osaka University.

Preparation of Materials. All reactions were carried out under a nitrogen atmosphere. Solvents of the highest purity grade were used as received. All reagents were purchased from commercial sources and used without purification. Compounds **4** and **DTS-Sn** were prepared by our previously reported procedure and ^{1}H NMR data of these compounds were in agreement with those previously reported.

Synthesis

*Synthesis of **2***: **1** (1.93 g, 10.0 mmol) in THF (10 mL) was added to lithium diisopropylamide (11 mmol) in THF (10 mL) at –78 °C. After stirring for 2 h, 1-iodohexane (3.39 g, 16.0 mmol) was added. After stirring for 0.5 h, the mixture was gradually warmed up to room temperature. The reaction mixture was quenched by addition of 2 M HCl aq., and the organic layer was separated. The aqueous layer was extracted with diethyl ether (Et_2O), and the combined organic layer was dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane) to give **2** as a colorless oil (1.88 g, 76%). This compound was used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.92-6.97 (m, 2H), 2.79 (td, J = 8.4, 2.4 Hz, 2H), 1.53-1.57 (m, 2H), 1.29-1.53 (m, 4H), 0.89 (m, 3H).

*Synthesis of **3d** and **3e***: A solution of hexyl magnesium chloride (2.27g, 12.0 mmol) in THF (4 mL) was added dropwise to **2** (1.11 g, 4.00 mmol) and $NiCl_2$(dppp) (216 mg, 0.398mmol) in THF (4 mL) at 0 °C. The mixture was warmed to 85 °C and stirred for overnight. The reaction mixture was quenched by water and 2 M HCl aq., and the organic layer was separated. The aqueous layer was extracted with diethyl ether (Et_2O). After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane) followed by distillation to afford **3d** (269 mg, 24%) and **3e** (393 mg, 50%). **3d**: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.79 (t, J = 6.8 Hz, 2H), 2.60 (t, J = 7.6 Hz, 4H), 1.50 (m, 4H), 1.29-1.38 (m, 8H), 1.30 (m, 4H), 0.89 (m, 6H). **3e**: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.89-6.96 (m, 1H), 6.80-6.88 (m, 2H), 2.60 (t, J = 7.6 Hz, 2H), 1.59 (m, 2H), 1.25-1.37 (m, 6H), 0.90 (m, 3H).

*Synthesis of **5a***: Compound **4** (1.47 g, 4.00 mmol) was dissolved with CH_2Cl_2 (10 mL), and degassed with nitrogen. Anhydrous aluminum trichloride ($AlCl_3$) (3.00 g, 22.5 mmol) was added at 0 °C. Benzene (10 mL) was then added dropwise to the stirred mixture at 0 °C. After stirring the reaction mixture at 0 °C for 2 h, it was poured into ice and extracted with chloroform ($CHCl_3$). The resulting organic layer was washed with water and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was washed by hexane and Et_2O, and further purification by GPC afforded **5a** as a light-yellow solid (298 mg, 39%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.31 (dd, J = 5.6, 3.2 Hz, 2H), 7.82 (dd, J = 7.6, 5.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 175.04, 158.21, 132.30, 124.86, 122.78, 121.16; MS (EI) m/z 372 [M^+]; HRMS (APCI) m/z 372.8349 (M^+) (M^+, Calcd 372.8351).

*Synthesis of **5b***. Compound **5b** was synthesized from **4** and **3b** with a yield of 23% by following the procedure used for the preparation of **5a**. Light-yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.48 (dd, J = 7.6, 5.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 177.6, 160.2, 150.2, 138.2, 132.8, 129.1; MS (EI) m/z 408 (M^+); HRMS (APCI) m/z 408.8166 ($[M]^+$) (M^+, Calcd 408.8163).

*Synthesis of **5c***. Compound **5c** was synthesized from **4** and **3c** with a yield of 18% by the isolation using column chromatography ($CHCl_3$) and further purification by GPC. Light-orange solid; ^{13}C NMR (100 MHz, $CDCl_3$, δ): 175.3, 147.2, 144.0, 131.5, 127.3, 117.5; MS (EI) m/z 443 (M^+); HRMS (APCI) m/z 444.7973 ($[M]^+$) (M^+, Calcd 444.7974).

*Synthesis of **5d***. Compound **5d** was synthesized from **4** and **3d** with a yield of 61% by the isolation using column chromatography (hexane:$CHCl_3$ = 1:1) and further purification by GPC. Light-yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 2.74 (t, J = 8.0 Hz, 4H), 1.42 (quintet, J = 6.4 Hz, 4H), 1.31-1.39 (m, 12H), 0.89 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 177.6, 160.2, 150.2, 138.2, 132.8, 129.1, 33.0, 31.7, 30.6, 29.0, 22.6, 14.1. MS (EI) m/z 576 (M^+); Anal. calcd for $C_{24}H_{26}Br_2F_2O_2S$: C, 49.98; H, 4.45; Found: C, 50.02; H, 4.55.

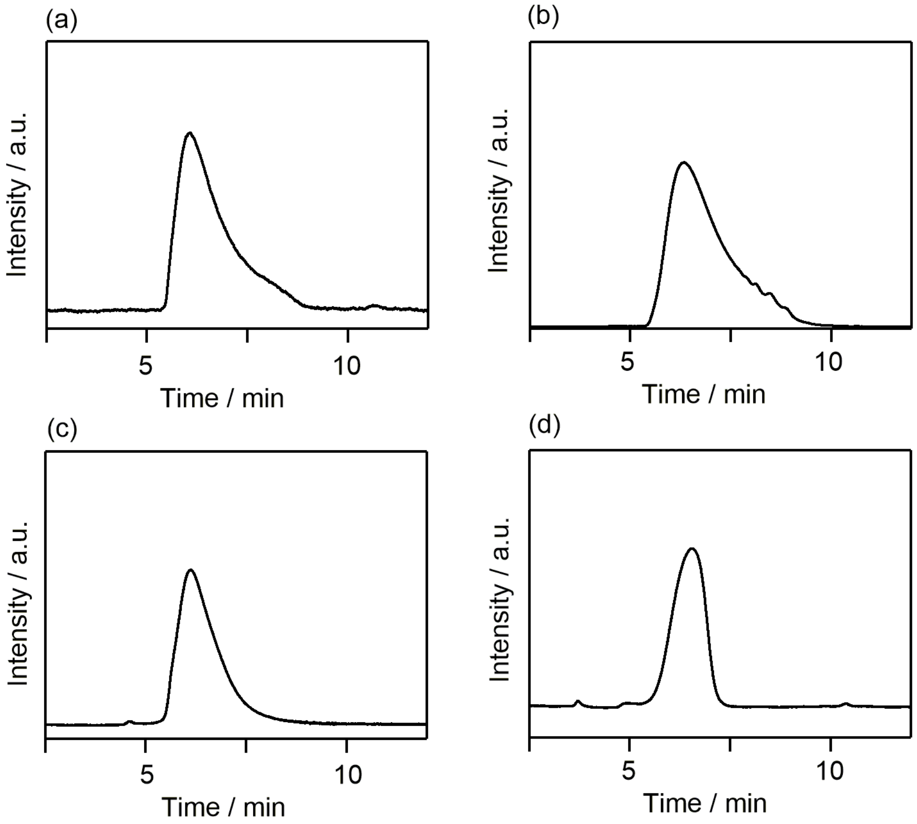
*Synthesis of **DTS-C₀***: **DTS-Sn** (145 mg, 0.194 mmol), **5a** (72 mg, 0.194 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (8.0 mg, 7.8 μmol), and P(o-tolyl)$_3$ (10.6 mg, 0.0350 mmol) were placed in a microtube and dissolved with toluene (2 mL). The mixture was then reacted in a microwave reactor at 180 °C for 40 min, and then cooled to room temperature. The polymer solution was precipitated into methanol at room temperature. The resulting purple-black solid was filtered into a Soxhlet thimble, and extracted with methanol, hexane, and $CHCl_3$ until the wash from each extraction became colorless. When there was no solid remaining in the thimble, the $CHCl_3$ fraction was concentrated. The copolymer solution was then poured into methanol at room temperature. The obtained precipitate was filtered, and dried under vacuum to yield **DTS-C_0** (75 mg, 61%). Black solid; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.41 (br, 2H), 7.82-7.94 (br, 4H), 1.37-1.45 (br, 14H), 1.08 (br, 4H), 0.85-0.87 (br, 16H); GPC ($CHCl_3$, 40 °C): M_n = 35.3 kg/mol, $Đ_M$ = 1.49.

*Synthesis of **DTS-$C_0(F_2)$***: **DTS-$C_0(F_2)$** was synthesized from **DTS-Sn** and **5b** with a yield of 70% by following the procedure used for the preparation of **DTS-C_0**. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.93 (br, 2H), 7.46-7.51 (br, 2H), 1.37-1.45 (br, 14H), 1.07 (br, 4H), 0.84-0.85 (br, 16H); GPC ($CHCl_3$, 40 °C): M_n = 31.6 kg/mol, $Đ_M$ = 1.62.

*Synthesis of **DTS-$C_0(F_4)$***: **DTS-$C_0(F_4)$** was synthesized from **DTS-Sn** and **5c** with a yield of 32% by following the procedure used for the preparation of **DTS-C_0**. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.92 (br, 2H), 1.33-1.50 (br, 14H), 1.08 (br, 4H), 0.85-0.91 (br, 16H); GPC ($CHCl_3$, 40 °C): M_n = 36.6 kg/mol, $Đ_M$ = 1.48.

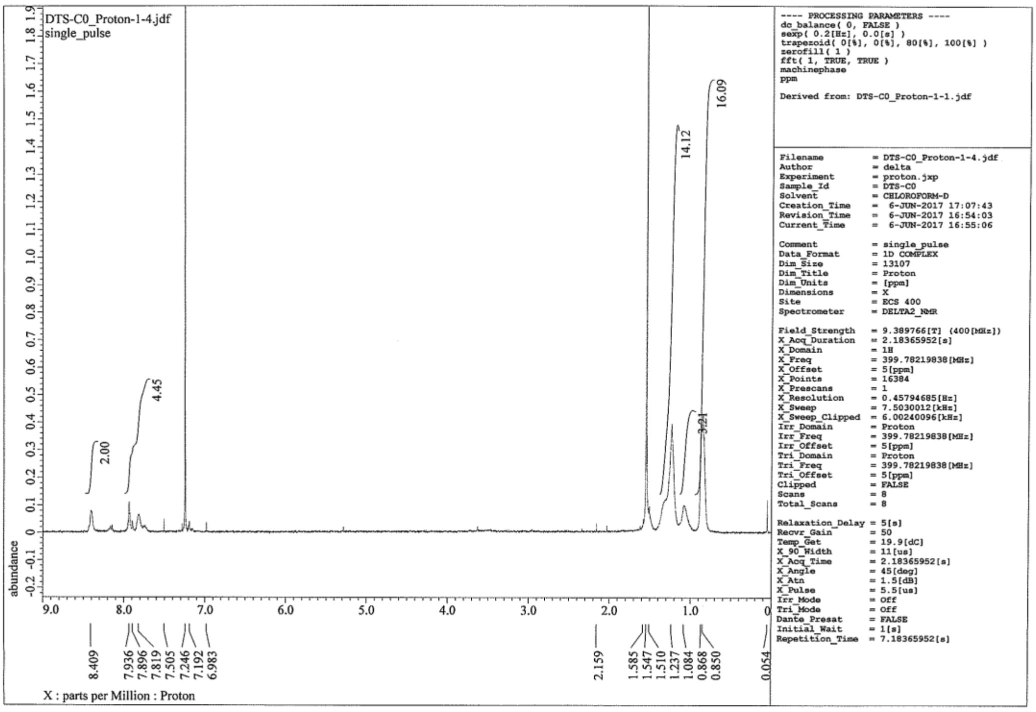
*Synthesis of **DTS-$C_6(F_2)$***: **DTS-$C_6(F_2)$** was synthesized from **DTS-Sn** and **5d** with a yield of 72% by following the procedure used for the preparation of **DTS-C_0**. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.91 (br, 2H), 2.77 (br, 4H), 1.21-1.80 (br, 28H), 1.08 (br, 4H), 0.82-0.90 (br, 24H); GPC ($CHCl_3$, 40 °C): M_n = 36.8 kg/mol, $Đ_M$ = 1.29.

GPC Charts



GPC charts for (a) **DTS-C$_0$**, (b) **DTS-C$_0$(F$_2$)**, (c) **DTS-C$_0$(F$_4$)**, and (d) **DTS-C$_6$(F$_2$)**.

NMR Spectra: ^{1}H NMR Spectrum of DTS-C$_0$



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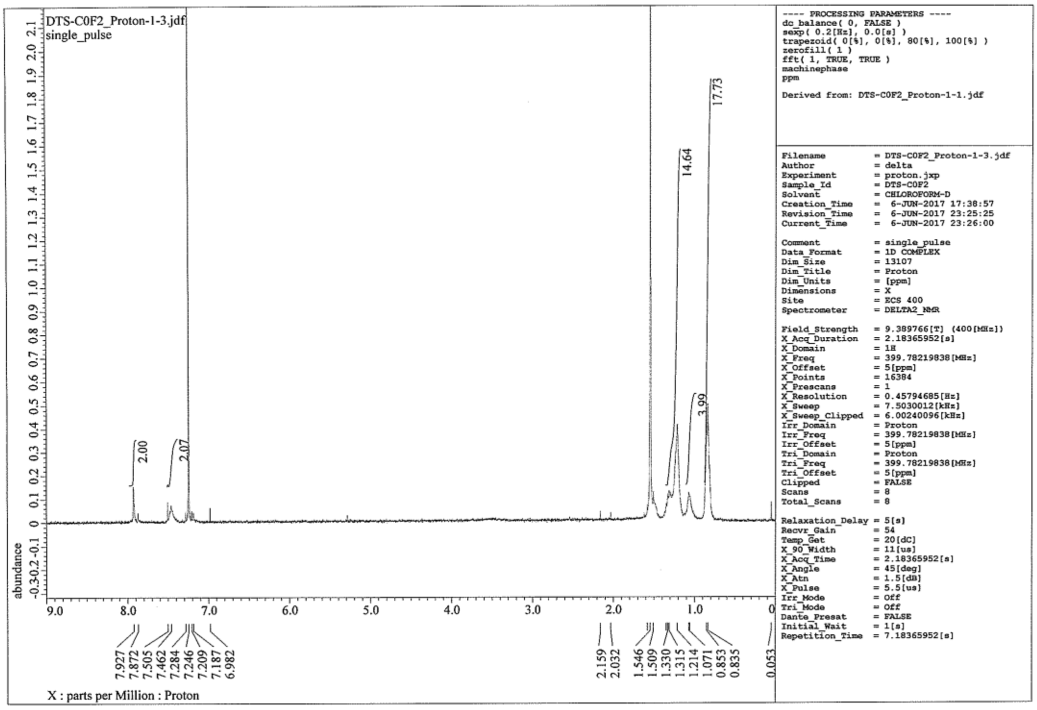
^{1}H NMR Spectrum of DTS-C$_0$(F$_2$)



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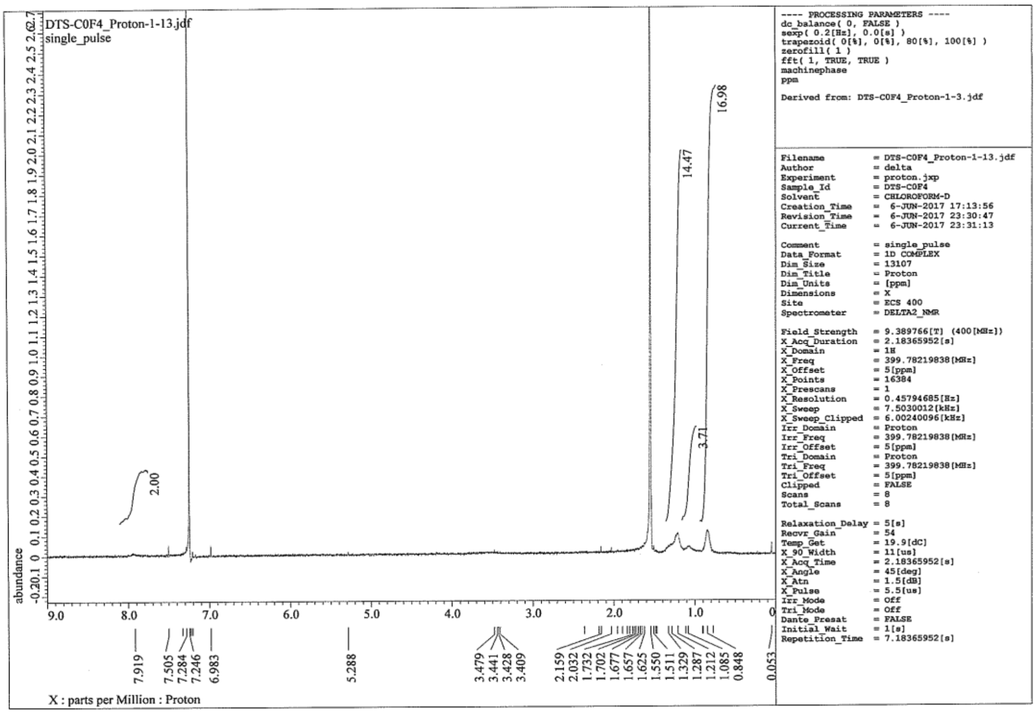

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Derived from: DTS-C0F4_Proton-1-3.jdf
```

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Filename          = DTS-C0F4_Proton-1-13.jdf
Author            = delta
Experiment        = proton.jxp
Sample_Id         = DTS-C0F4
Solvent           = CHLOROFORM-D
Creation_Time     =  6-JUN-2017 17:13:56
Revision_Time     =  6-JUN-2017 23:30:47
Current_Time      =  6-JUN-2017 23:31:13

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECS 400
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.389766[T] (400[MHz])
X_Acq_Duration    = 2.18365952[s]
X_Domain          = 1H
X_Freq            = 399.78219838[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.45794685[Hz]
X_Sweep           = 7.5030012[kHz]
X_Sweep_Clipped   = 6.00240096[kHz]
Irr_Domain        = Proton
Irr_Freq          = 399.78219838[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = Proton
Tri_Freq          = 399.78219838[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay = 5[s]
Recvr_Gain        = 54
Temp_Get          = 19.9[dC]
X_90_Width        = 11[us]
X_Acq_Time        = 2.18365952[s]
X_Angle           = 45[deg]
X_Atn             = 1.5[dB]
X_Pulse           = 5.5[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 7.18365952[s]
```
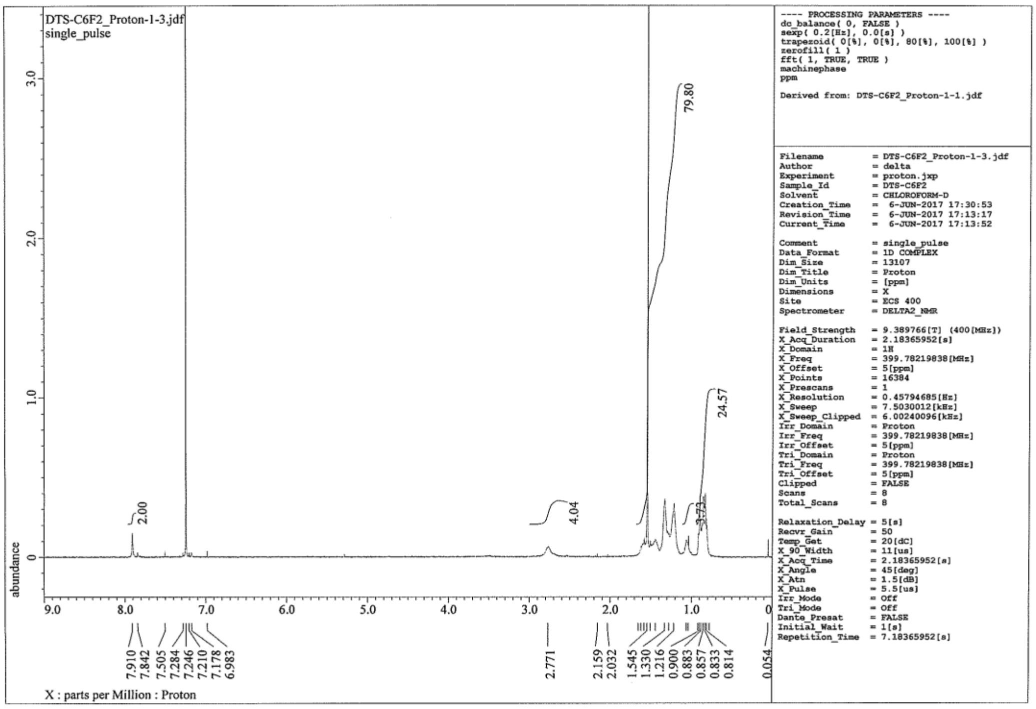

^{1}H NMR Spectrum of DTS-$C_6(F_2)$



```
---- PROCESSING PARAMETERS ----
dc_balance( 0, FALSE )
sexp( 0.2[Hz], 0.0[s] )
trapezoid( 0[%], 0[%], 80[%], 100[%] )
zerofill( 1 )
fft( 1, TRUE, TRUE )
machinephase
ppm

Derived from: DTS-C6F2_Proton-1-1.jdf
```

```
Filename          = DTS-C6F2_Proton-1-3.jdf
Author            = delta
Experiment        = proton.jxp
Sample_Id         = DTS-C6F2
Solvent           = CHLOROFORM-D
Creation_Time     =  6-JUN-2017 17:30:53
Revision_Time     =  6-JUN-2017 17:13:17
Current_Time      =  6-JUN-2017 17:13:52

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECS 400
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.389766[T] (400[MHz])
X_Acq_Duration    = 2.18365952[s]
X_Domain          = 1H
X_Freq            = 399.78219838[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.45794685[Hz]
X_Sweep           = 7.5030012[kHz]
X_Sweep_Clipped   = 6.00240096[kHz]
Irr_Domain        = Proton
Irr_Freq          = 399.78219838[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = Proton
Tri_Freq          = 399.78219838[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay = 5[s]
Recvr_Gain        = 50
Temp_Get          = 20[dC]
X_90_Width        = 11[us]
X_Acq_Time        = 2.18365952[s]
X_Angle           = 45[deg]
X_Atn             = 1.5[dB]
X_Pulse           = 5.5[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 7.18365952[s]
```

Photovoltaic Device Fabrication

Organic photovoltaic devices were prepared with a structure of ITO/PEDOT:PSS/active layer/Ca/Al. ITO-coated glass substrates were first cleaned by ultrasonication in toluene, acetone, water, and 2-propanol for 10 min, respectively. ITO-coated glass substrates were then activated by ozone treatment for 1 h. PEDOT:PSS was spin-coated on the ITO surface at 3000 rpm for 1 min and dried at 135 °C for 10 min. The active layers were prepared from 30 mg mL^{-1} solution of materials in *o*-DCB with 3% DIO. The active layers were then prepared by spin-coating on the ITO/PEDOT:PSS electrode at 800 rpm for 1 min in a glove box. The typical thickness of the active layer was 80–100 nm. Ca and Al electrodes were evaporated on the top of active layer through a shadow mask to define the active area of the devices (0.09 cm^2) under a vacuum of 10^{-5} Pa to a thickness of 30, 100 nm determined by a quartz crystal monitor. After sealing the device from the air, the photovoltaic characteristics were measured in air under simulated AM 1.5G solar irradiation (100 mW cm^{-2}) (SAN-EI ELECTRIC, XES-301S). The current density–voltage characteristics of photovoltaic devices were measured by using a KEITHLEY 2400 source meter. The EQE spectra were measured by using a Soma Optics Ltd. S-9240. The thickness of active layer was determined by KLA Tencor Alpha-step IQ.

Optimized **DTS-C$_0$(F$_2$)**:PC$_{71}$BM-based photovoltaic devices were prepared with a structure of ITO/PEDOT:PSS/**DTS-C$_0$(F$_2$)**:PC$_{71}$BM/Ba/Al. ITO-coated glass substrates were first cleaned by ultrasonication in water, acetone, and 2-propanol for 5 min, respectively, and then dried at 140 °C for 10 min. ITO-coated glass substrates were then activated by ozone treatment for 20 min. PEDOT:PSS was spin-coated on the ITO surface at 2000 rpm for 10 s then 4000 rpm 60 s and dried at 140 °C for 10 min. The active layers were prepared from 33 mg mL^{-1} solution of materials in *o*-DCB with 3% DIO. The active layers were then prepared by spin-coating on the ITO/PEDOT:PSS electrode at 800 rpm for 1 min in a glove box. Then, MeOH (20 μL) was spin-coated on the active layer at 1500 rpm for 2 min. The typical thickness of the active layer was 90–110 nm. Ba and Al electrodes were evaporated on the top of active layer through a shadow mask to define the active area of the devices (0.04 cm^2) under a vacuum of 10^{-7} mbar to a thickness of 5, 100 nm determined by a quartz crystal monitor. The photovoltaic characteristics were measured under nitrogen atmosphere using Glovescan.

SCLC Measurements

Double-carrier, Hole-only and electron-only devices were prepared with a structure of Au (30 nm)/PEDOT:PSS (25 nm)/**DTS-C$_0$(F$_2$)**:PC$_{71}$BM/Ba (5 nm)/Al (100 nm), Au (30 nm)/PEDOT:PSS (25 nm)/**DTS-C$_0$(F$_2$)**:PC$_{71}$BM/MoO$_3$ (10 nm)/Al (100 nm), and Al (30 nm)/**DTS-C$_0$(F$_2$)**:PC$_{71}$BM/Ba (5 nm)/Al (100 nm), respectively. Glass substrates were first cleaned by ultrasonication in water, acetone, and 2-propanol for 5 min, respectively, and then dried at 140 °C for 10 min. ITO-coated glass substrates were then activated by ozone treatment for 20 min. PEDOT:PSS was spin-coated on the glass surface at 2000 rpm for 10 s then 4000 rpm 60 s and then dried at 140 °C for 10 min. The active layers were prepared from 33 mg mL^{-1} solution of materials in *o*-DCB with 3% DIO. MoO_3, Ba, and Al electrodes were evaporated on the top of active layer through a shadow mask to define the active area of the devices (0.01 cm^2) under a vacuum of 10^{-7} mbar to a thickness of 10, 5, 100 nm, respectively, which was determined by a quartz crystal monitor. The carrier mobilities of these devices were calculated by the following equation:

$$J = \frac{9}{8}\varepsilon\varepsilon_0\mu\frac{V^2}{d^3}$$

where ε, ε_0, μ, and d are the dielectric constant of the active layer, the permittivity of free space, the carrier mobility, and the measured thickness of active layer, respectively. We used the values of $\varepsilon = 3$, $\varepsilon_0 = 8.8 \times 10^{-12}$.

SFE Estimation

The acceptor films were prepared on the quartz substrate by spin-coating using 10 mg mL^{-1} $CHCl_3$ solution (same as UV-vis absorption and emission spectra of films). The contact angles of the film surface were measured by a NiCK LSE-ME1 using 50 μL of proving liquids of distilled water and glycerol. SFEs were estimated from the simultaneous equations of following relation.

$$\gamma_L(1 + cos\theta) = 2\sqrt{\gamma_S^d\gamma_L^d} + \sqrt{\gamma_S^p\gamma_L^p}$$

where θ, γ_L, and γ_S are the contact angle, surface energy of liquid, and surface energy of surface, respectively.