

Supporting information

Simple-Structure Small Molecular Acceptors Based on Benzodithiophenedione Core: Synthesis, Optoelectronic and Photovoltaic Properties

Mengbing Zhu, Xiankang Yu , Jingwei Huang, Hao Xia, Jianing Zhu, Wenhong Peng,

Hua Tan *, Weiguo Zhu *

School of Materials Science and Engineering, Jiangsu Engineering Laboratory of Light-Electricity-Heat Energy-Converting Materials and Applications, Jiangsu Collaborative Innovation Center of Photovoltaic Science and Engineering, Jiangsu Key Laboratories of Environment-Friendly Polymers, National Experimental Demonstration Center for Materials Science and Engineering, Changzhou University, Changzhou 213164, China

Corresponding author:

W. G. Zhu, E-mail: zhuwg18@126.com

H. Tan, E-mail: tanhua815@126.com

1. Instrumentations and characterization

^1H NMR spectra were tested with a Bruker AV-400, utilizing deuterated chloroform (CDCl_3) as solvent and tetramethylsilane (TMS) as internal standard. Molecular mass (MS) was measured with a Bruker Biflex III MALDI-TOF spectrometric instrument. Thermal stability was evaluated by the thermogravimetric analyses (TGA) on a Netzsch TG 209 analyzer under protection of nitrogen atmosphere at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. Crystallinity was assessed by differential scanning calorimetry (DSC) on a PE DSC8500 instrument under a nitrogen atmosphere at a heating or cooling rate of $10\text{ }^\circ\text{C min}^{-1}$ in a $50 \sim 300\text{ }^\circ\text{C}$ temperature range. The theoretical study was carried out through the density functional theory (DFT). It was approximated by the B3LYP employing the 6-31G** basis set in Gaussian 09. A methyl group was used to replace each long alkyl chain for simplified calculation. UV-vis spectra were recorded by a Shimadzu UV-1800 spectrometer. Cyclic voltammetry (CV) was tested on a CHI 630E electrochemical work station by a three-electrode electrochemical cell in a 0.1 M tetra(*n*-butyl) ammonium hexafluoro-phosphate (Bu_4NPF_6) solution with a scan rate of 100 mV s^{-1} at ambient temperature under an argon atmosphere. In this three-electrode system, platinum wire and Ag/AgCl (0.1 M) electrode were respectively used as a counter electrode and a reference electrode. The Pt disk with organic thin film, formed by drop-casting SMAs chloroform (CF) solution, was used as the working electrode. The energy levels of the frontier molecular orbitals were calculated by the following formulas.

$$E_{\text{HOMO}} = -(E_{\text{ox}}^{\text{onset}} - E_{(\text{ferrocene})}^{\text{onset}} + 4.8)\text{ eV}$$

$$E_{\text{LUMO}} = -(E_{\text{red}}^{\text{onset}} - E_{(\text{ferrocene})}^{\text{onset}} + 4.8)\text{ eV}$$

In the formulas, $E_{\text{ox}}^{\text{onset}}$ and $E_{\text{red}}^{\text{onset}}$ represent the onset oxidation and reduction potentials. $E_{(\text{ferrocene})}^{\text{onset}}$ is the potential of ferrocene/ferrocenium (Fc/Fc^+) couple versus Ag/AgCl, which is measured to be 0.46 V . Film surface morphologies were recorded with a Veeco-DI Multimode NS-3D atomic force microscope (AFM) in a tapping mode under normal air condition and room temperature. The contact angle tests were performed on a Dataphysics OCA40 Micro surface contact angle analyzer.

The surface energy of the polymers donor and acceptors were characterized and calculated by the contact angles of the two probe liquids (water and diiodomethane) using the Wu model.

2. Fabrication and characterization of organic solar cells

Bulk heterojunction solar cells were fabricated with the following conventional structure: ITO/PEDOT:PSS/active layer/PDINO/Al. ITO substrates were cleaned with isopropyl alcohol, detergent water, deionized water, acetone and isopropyl alcohol in an ultrasonic bath sequentially for 15 min, and then dried in an oven at 85 °C for 12 hours. The PEDOT:PSS was spin-coated at 4000 r.p.m. onto the ITO surface and thermal annealed (150 °C) for 15 min in air, and the thickness of PEDOT:PSS films are all about 30 nm. Then the PEDOT:PSS-coated substrates were transferred into a nitrogen-filled glove box. A 6 mg mL⁻¹ chloroform solution of donor:acceptor was spin-coated at 2000 r.p.m. upon PEDOT:PSS layer. The PDINO was spin-coated at 3000 r.p.m. onto the active layer surface. Then evaporated 100-nm-thick Al on the devices with a shadow mask of 6 mm² under the pressure of ca. 10⁻⁴ Pa successively. The current density-voltage (*J-V*) characteristics of the devices were measured on a computer-controlled Keithley 2420 Source Measure Unit under illumination of AM 1.5 G solar simulator (Newport, 100 mW cm⁻², calibrated by a silicon reference cell). The external quantum efficiencies (EQE) of solar cells were analyzed using a certified Newport incident photon conversion efficiency (IPCE) measurement system (Model 66902).

The thickness of active layers in the photovoltaic devices was measured on a Veeco Dektak 150 profilometer. SCLC mobility was measured using a diode configuration of ITO/PEDOT:PSS/active layer/MoO₃/Al for the hole-only cells and ITO/ZnO/active layer/PFN-Br/Al for the electron-only cells by taking the dark current density in the range of 0 - 2 V and fitting the results to a space charge limited form, where SCLC is described by the following formula.

$$J = \frac{9\epsilon_0\epsilon_r\mu_0V^2}{8L^3} \exp(0.89\beta\sqrt{\frac{V}{L}})$$

In this formula, *J* is the current density, *L* is the film thickness of the active layer, μ_0

is the hole or electron mobility, ϵ_r is the relative dielectric constant of the transport medium, ϵ_0 is the permittivity of free space (8.85×10^{-12} F m⁻¹), V ($= V_{\text{appl}} - V_{\text{bi}}$) is the internal voltage in the device, where V_{appl} is the applied voltage to the device and V_{bi} is the built-in voltage due to the relative work function difference of the two electrodes.

3. Synthesis and characterizations

All solvents and reagents were purchased from commercial sources and were used without further purification unless stated otherwise. Anhydrous tetrahydrofuran (THF) was prepared by dryness and distillation.

Synthesis of compound 2

In a 100 mL two-neck round-bottom flask, n-BuLi (3 mL, 2.5 M in hexane) was added slowly to the solution of 3-undecylthieno[3,2-b]thiophene (2 g, 6.79 mmol) and anhydrous THF (30 mL) at -78 °C through funnel. The mixture was stirred at the same temperature for 2 h and then tributyltin chloride (2.43 g, 1 M in hexane) was added by syringe. The mixture was allowed to warm to room temperature and stirred overnight, then was poured into water (150 mL). The resulting mixture was extracted with CH₂Cl₂ and the organic phases were combined, then dried over with anhydrous MgSO₄. The solvents were removed off under reduced pressure and a yellow viscous liquid of 3.85 g was obtained, which was used in next step without further purification. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.23 (s, 1H), 6.95 (s, 1H), 2.70-2.74 (t, $J = 7.2, 8.0$ Hz, 2H), 1.77-1.73 (d, $J = 6.8, 7.6$ Hz, 2H), 1.64 – 1.54 (m, 10H), 1.36-1.32 (s, 18H), 1.15 – 1.10 (m, 6H), 0.92 – 0.86 (m, 12H). ¹³C NMR (75 MHz, CDCl₃) δ 177.60 (s), 153.54 (s), 143.02 (s), 142.51 (s), 138.77 (s), 135.17 (s), 134.32 (s), 133.10 (s), 123.88 (s), 123.49 (s), 77.65 – 76.84 (m), 76.61 (s), 41.22 (s), 33.69 (s), 32.76 (s), 31.94 (s), 30.09 – 29.24 (m), 28.74 (d, $J = 14.0$ Hz), 26.01 (s), 23.04 (s), 22.72 (s), 14.16 (d, $J = 2.6$ Hz), 10.90 (s).

Synthesis of compound 3

In a 100 mL two-neck round-bottom flask, compound 1 (500 mg, 0.83 mmol), compound 2 (1.4529 g, 2.49 mmol), and Pd₂(dba)₃ (38 mg, 0.04 mmol), tri(o-tolyl)

phosphine (50 mg, 0.16 mmol) was added, and then degassed toluene was injected into the mixture. The flask was evacuated and back-filled with N₂ three times. The resulting solution was stirred at 100 °C for 2 h under the N₂ atmosphere. After being cooled to room temperature, the mixture was poured into water (150 mL), and extracted with CH₂Cl₂. The organic phases were combined, and then dried over with anhydrous MgSO₄. The solvents were then removed under reduced pressure. The yellow residue was purified by silica gel chromatography, eluting with PE: CH₂Cl₂ (10:1, v/v) to give yellow liquid (733 mg, 85.8 %). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.08 (s, 2H), 7.06 (s, 2H), 3.30 (d, *J* = 7.0 Hz, 4H), 2.74 (t, *J* = 7.5, 7.5 Hz, 4H), 1.86 (m, 2H), 1.78 (m, 6H), 1.65 (m, 2H), 1.46 – 1.30 (m, 44H), 0.95 – 0.89 (m, 18H). ¹³C NMR (75 MHz, CDCl₃) δ 182.42 (s), 177.07 (s), 154.43 (s), 144.82 (s), 143.84 (s), 143.25 (s), 142.15 (s), 140.35 (s), 139.88 (s), 134.18 (s), 132.55 (s), 123.62 (s), 77.68 – 76.87 (m), 76.64 (s), 41.15 (s), 33.74 (s), 32.76 (s), 31.92 (s), 30.03 (s), 29.88 – 29.21 (m), 28.79 (s), 28.33 (s), 26.04 (s), 23.02 (s), 22.71 (s), 14.16 (d, *J* = 3.1 Hz), 10.89 (s). MS(MALDI-TOF) (*m/z*) of C₆₀H₈₄O₂S₆ for [M]⁺: calcd. 1028.48; found 1029.56.

Synthesis of compound 4

In a 50 mL two-necked flask, the compound **3** (500 mg, 0.49 mmol) was dissolved in DMF (25 mL) under an argon atmosphere, POCl₃ (1.33 g, 8.70 mmol) was added drop wise into the mixture solution at 0 °C and stirred for 2 h, then the mixture was heated up to 65 °C overnight. After reaction finished, the mixture was pour into cold NaHCO₃ aqueous solution. The crude product was extracted with ethylacetate and washed with NaCl aqueous solution. After removing the solvent, silica gel column chromatography was used to purify the product with the mixture of PE:CH₂Cl₂ (1:1, v/v) as the eluent. The pure compound **4** was obtained as orange oil (457 mg, 86.7 %). ¹H NMR (500 MHz, Chloroform-*d*) δ 10.13 (s, 2H), 8.06 (s, 2H), 3.32 – 3.29 (dd, *J* = 6, 1.6 Hz, 4H), 3.14 (t, *J* = 6, 6 Hz, 4H), 1.87 – 1.83 (m, 4H), 1.78 – 1.75 (m, 2H), 1.43 – 1.30 (m, 36H), 0.93 (m, 16H), 0.87 (m, 12H), 0.84 (m, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 145.78 (s), 140.87 (s), 139.66 (s), 134.57 (s), 127.51 – 126.87 (m),

126.57 (s), 121.74 (s), 121.46 (s), 119.93 (s), 119.52 (s), 77.68 – 76.87 (m), 76.64 (s), 32.12 (s), 31.64 (s), 30.15 (s), 29.81 (d, $J = 24.5$ Hz), 29.30 – 28.74 (m), 28.38 (d, $J = 5.5$ Hz), 27.82 (d, $J = 13.5$ Hz), 27.34 (s), 26.94 (s), 22.58 (d, $J = 10.2$ Hz), 14.08 (s), 13.72 (s), 13.26 (d, $J = 7.9$ Hz), 11.01 (d, $J = 8.4$ Hz), 8.65 (d, $J = 7.9$ Hz), 0.04 (s). MS(MALDI-TOF) (m/z) of $C_{62}H_{84}O_4S_6$ for $[M]^+$: calcd. 1084.47; found 1085.47.

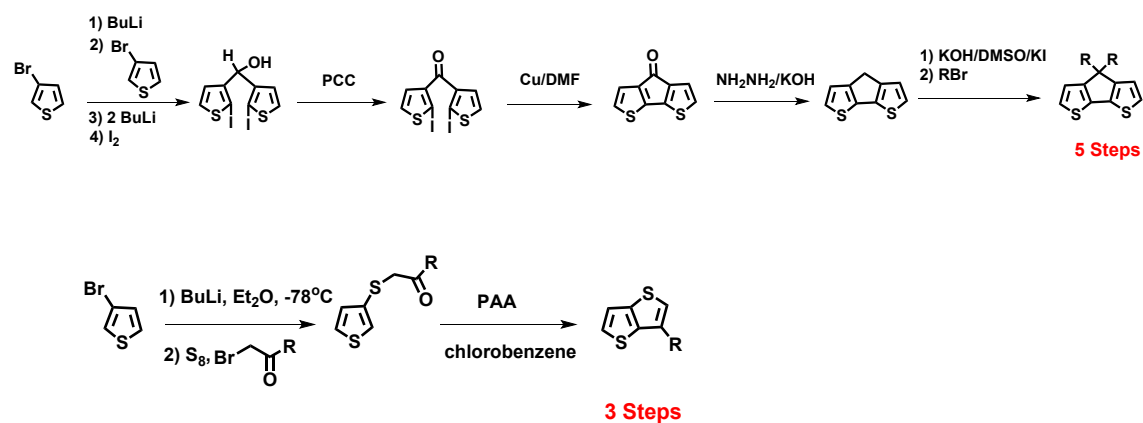
Synthesis of BDDTTIC

The compound **4** (100 mg, 0.09 mmol) and 2-(3-oxo-2,3-dihydro1H-inden-1-ylidene)malononitrile (89 mg, 0.46 mmol) were dissolved in $CHCl_3$ (15 mL) and pyridine (0.2 mL). The reaction was stirred at 65 °C for 5 h to precipitate crude product into methanol, vacuum filter after 3h. Then, the product was purified by silica gel using a mixture of hexane/dichloromethane as the eluent, and recrystallization from a mixed solution of chloroform and methanol to give a black solid (115mg, 86.8 %). Mp: 256-258 °C. 1H NMR (400 MHz, Chloroform-*d*) δ 8.72 (s, 2H), 8.37-8.35 (d, $J = 7.7$ Hz, 2H), 7.92-7.90 (d, $J = 7.2$ Hz, 2H), 7.84 (s, 2H), 7.77-7.69 (dt, $J = 19.5, 7.0$ Hz, 4H), 3.39 – 3.14 (m, 4H), 3.09 – 3.04 (m, 4H), 1.80 (d, $J = 27.4$ Hz, 6H), 1.46 – 1.25 (m, 48H), 1.01 (t, $J = 6.3, 6.3$ Hz, 6H), 0.93 (t, $J = 5.8, 5.8$ Hz, 6H), 0.85 (t, $J = 6.7, 6.7$ Hz, 6H). MS(MALDI-TOF) (m/z) of $C_{86}H_{92}N_4O_4S_6$ for $[M]^+$: calcd. 1436.54; found 1437.26.

Synthesis of BDDTTIC-4F

The synthetic step of BDDTTIC-4F is similar to that of BDDTTIC. BDDTTIC-4F was obtained as a black solid (117 mg, 84.5%). Mp: 283-285 °C. 1H NMR (400 MHz, Chloroform-*d*) δ 8.82 (s, 2H), 8.35 (d, $J = 8.0$ Hz, 2H), 7.86 (s, 2H), 7.54 (t, $J = 6.5, 6.5$ Hz, 2H), 3.38 (m, $J = 3.3$ Hz, 2H), 3.24 (m, 2H), 3.01 (t, $J = 7.6, 7.6$ Hz, 4H), 1.84 (s, 2H), 1.74 (s, 4H), 1.39 (m, 48H), 1.03 (t, $J = 7.2, 7.2$ Hz, 6H), 0.94 (t, $J = 6.4, 6.4$ Hz, 6H), 0.86 (t, $J = 6.0, 6.0$ Hz, 6H). MS(MALDI-TOF) (m/z) of $C_{86}H_{88}F_4N_4O_4S_6$ for $[M]^+$: calcd. 1508.51; found 1509.31.

4. Supplementary Figures and Tables



Scheme S1. Synthesis routes of alkyl CPDT and alkyl TT

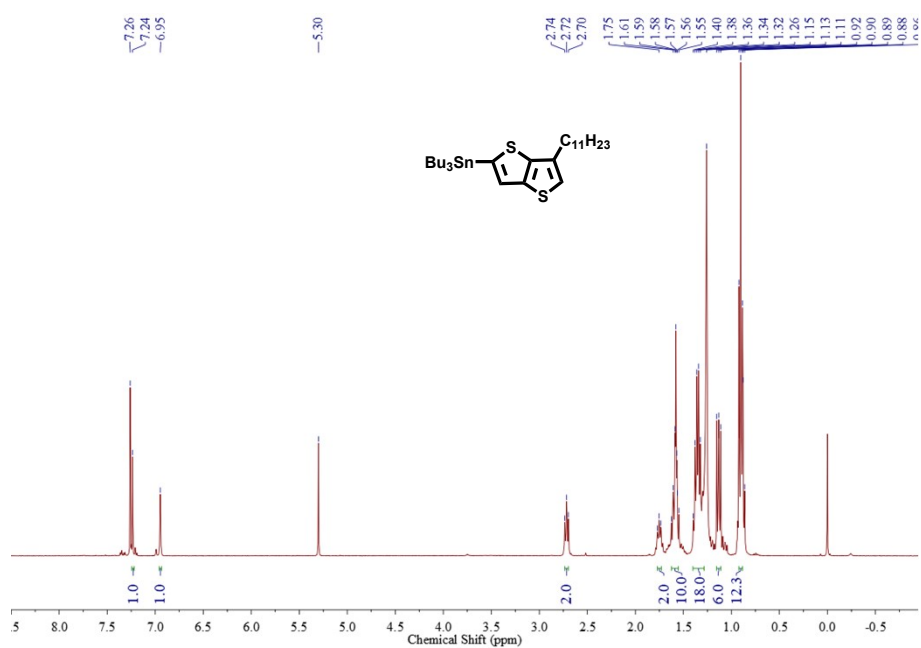


Figure S1. ^1H NMR spectrum of compound **2**.

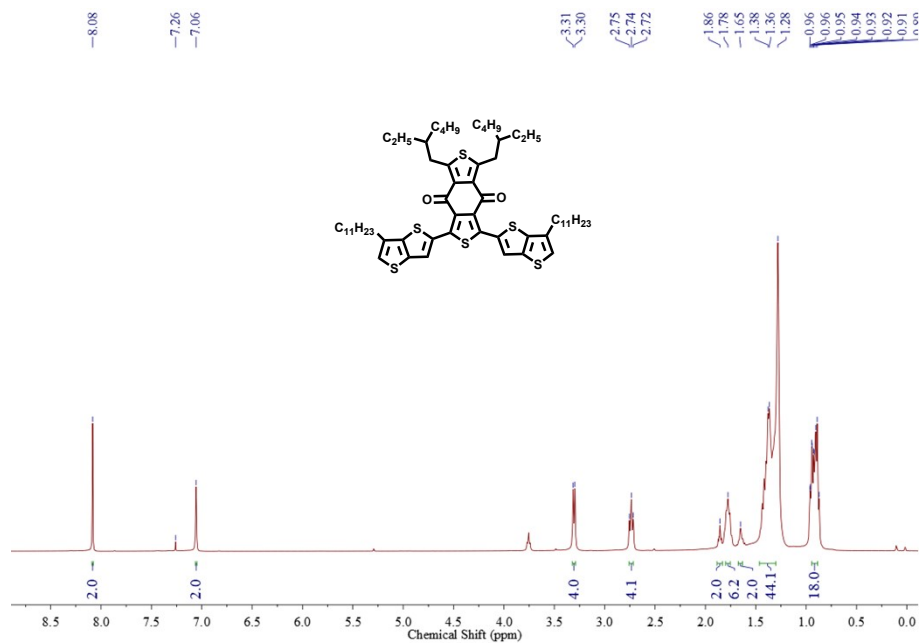


Figure S2. ^1H NMR spectrum of compound 3

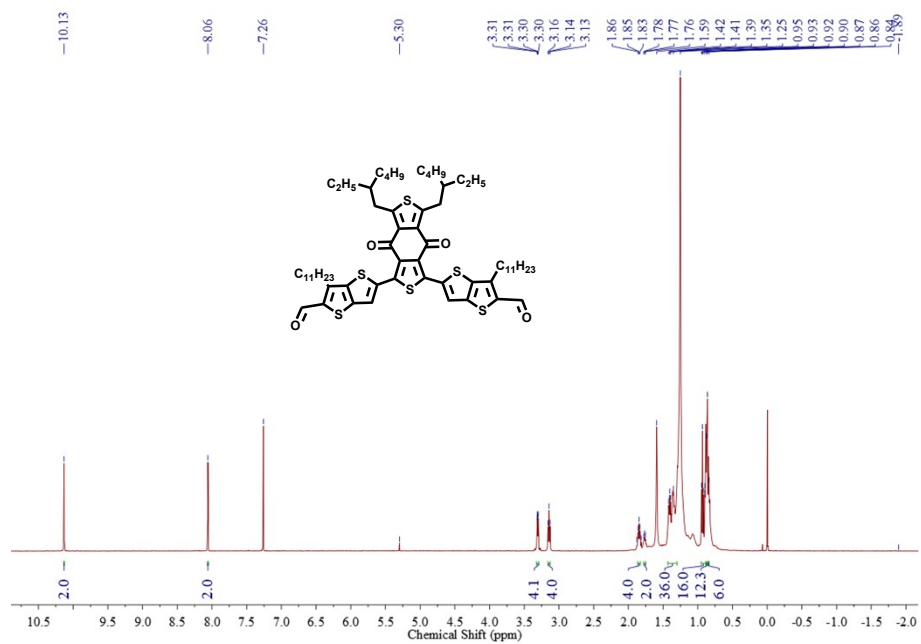


Figure S3. ^1H NMR spectrum of compound 4.

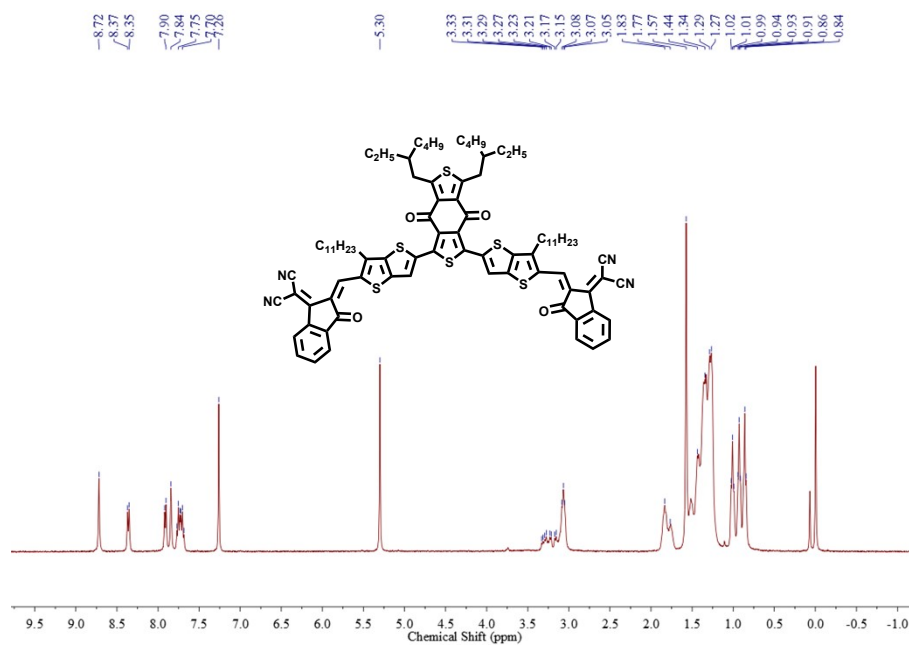


Figure S4. ^1H NMR spectrum of BDDTTIC.

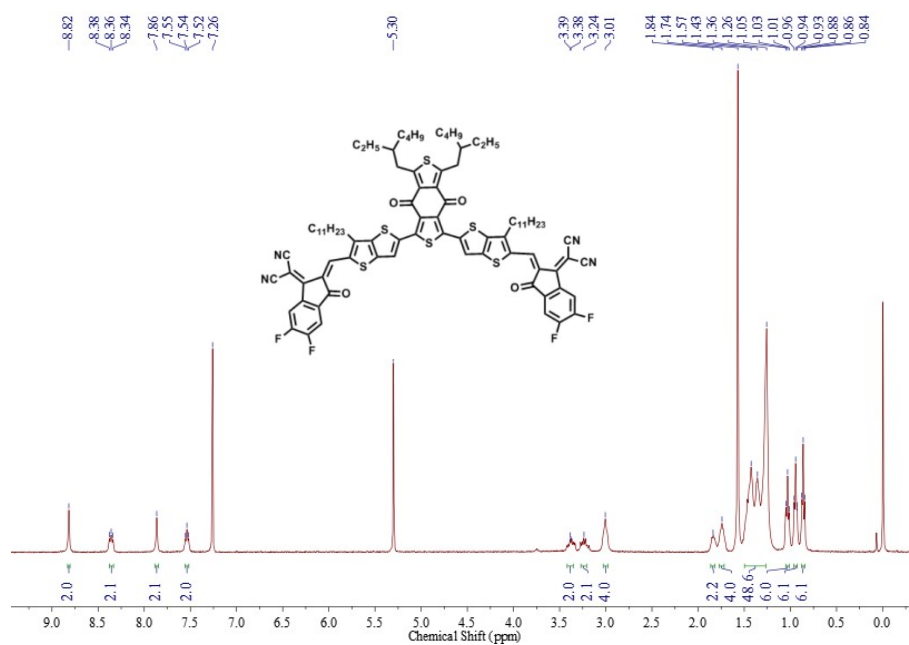


Figure S5. ^1H NMR spectrum of BDDTTIC-4F.

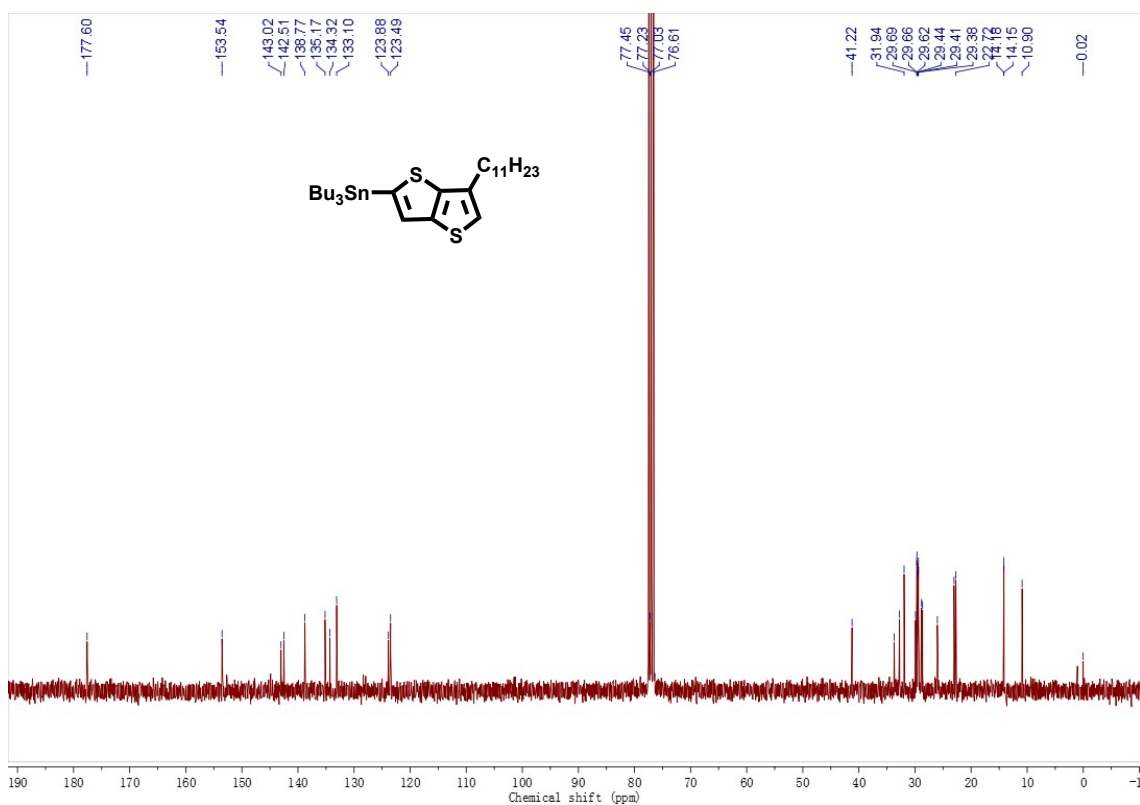


Figure S6. ¹³C NMR spectrum of compound 2.

Figure S7. ¹³C NMR spectrum of compound 3

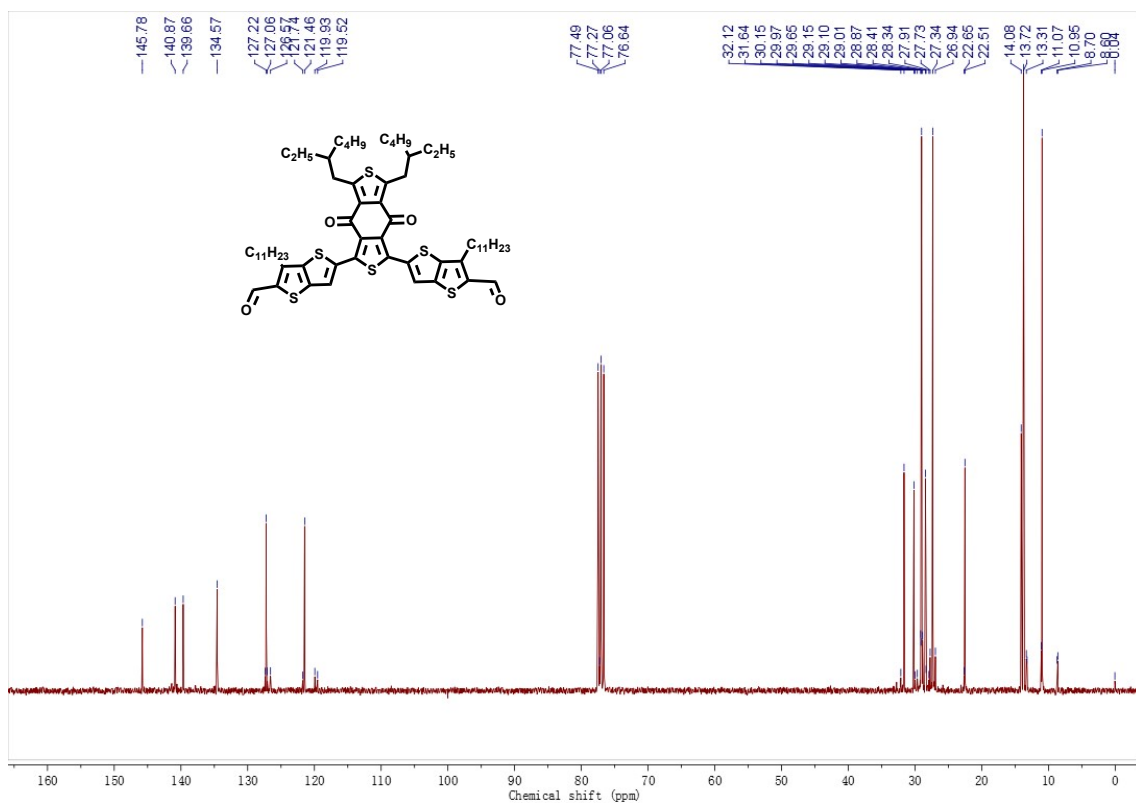


Figure S8. ¹³C NMR spectrum of compound 4

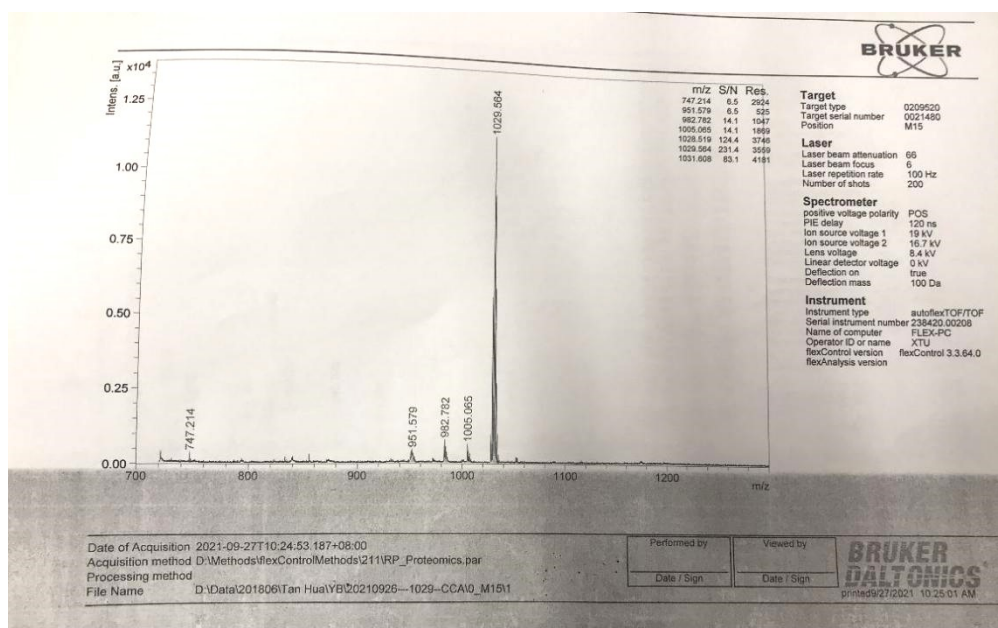


Figure S9. TOF-MS of compound 3

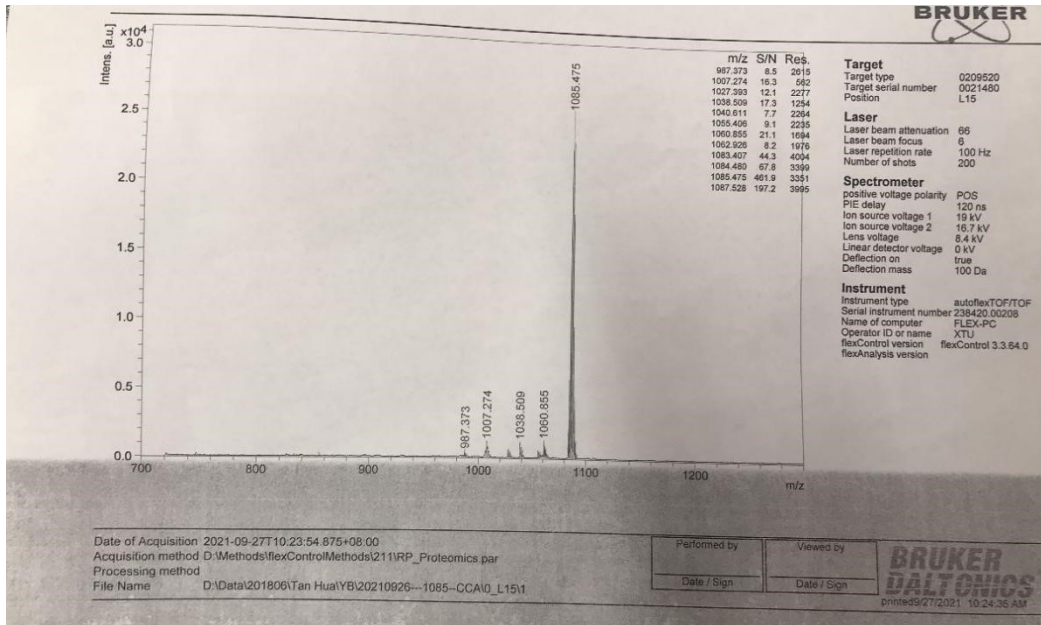


Figure S10. TOF-MS of compound 4

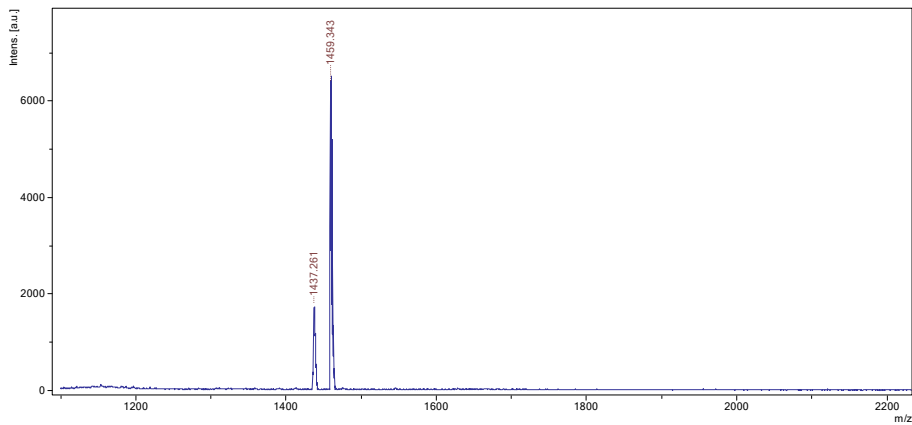


Figure S11. TOF-MS of BDDTTIC

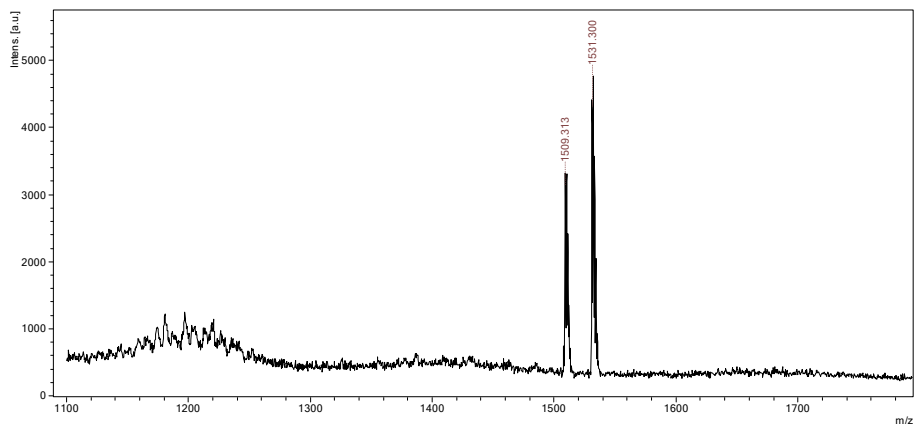


Figure S12. TOF-MS of BDDTTIC-4F.

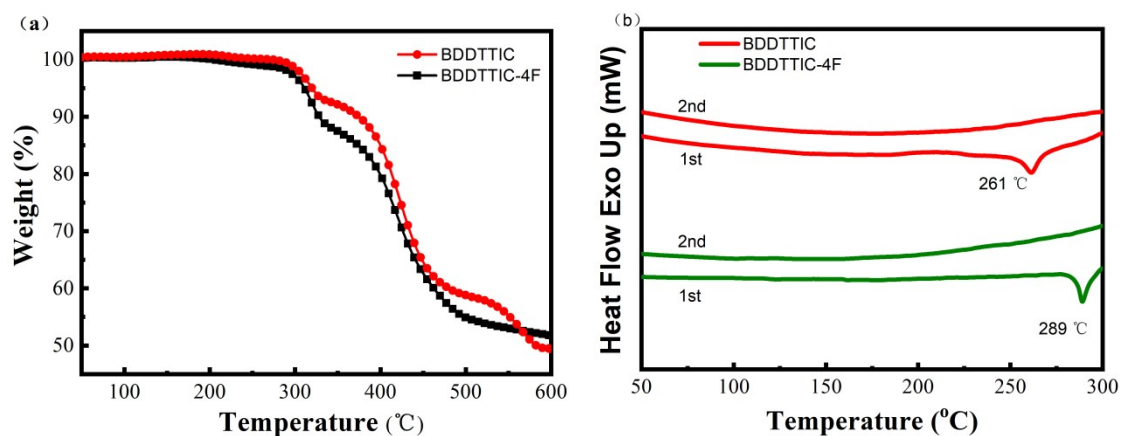


Figure S13. (a) Thermal gravimetric analysis (TGA) curve and (b) Differential scanning calorimeter (DSC) curve of the BDDTTIC and BDDTTIC-4F solid powders.

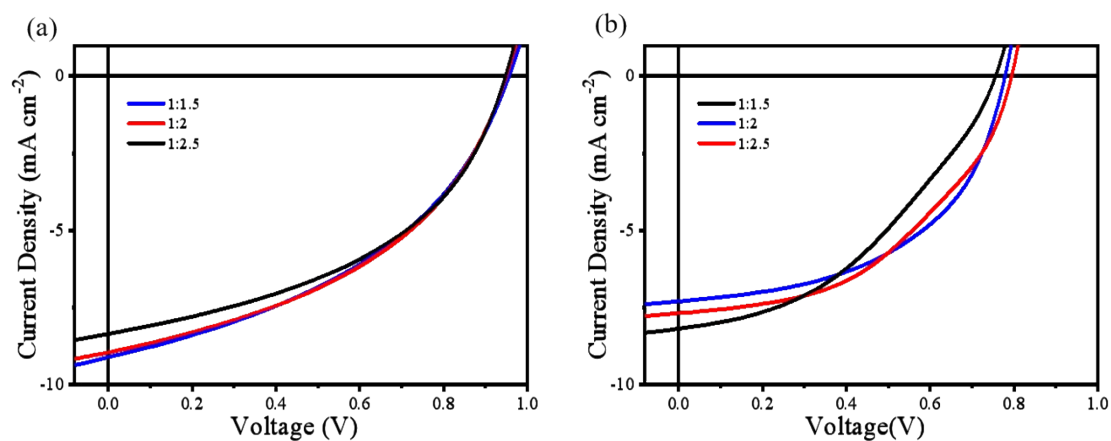


Figure S14. Photovoltaic properties of OSCs with different D/A ratios based on (a) PM6:BDDTTIC and (b) PM6:BDDTTIC-4F blend films.

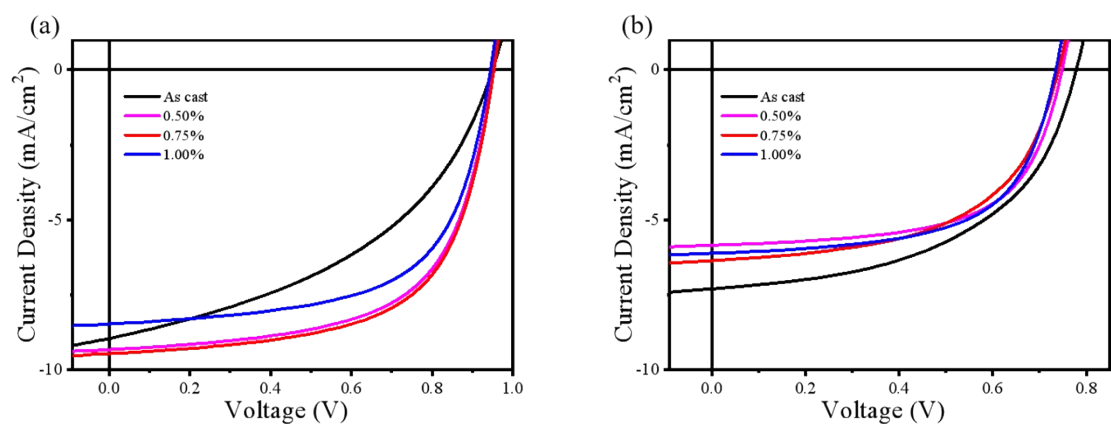


Figure S15. Photovoltaic properties of OSCs at different 1-chloronaphthalene ratio based on the (a) PM6:BDDTTIC and (b) PM6: BDDTTIC-4F blend films.

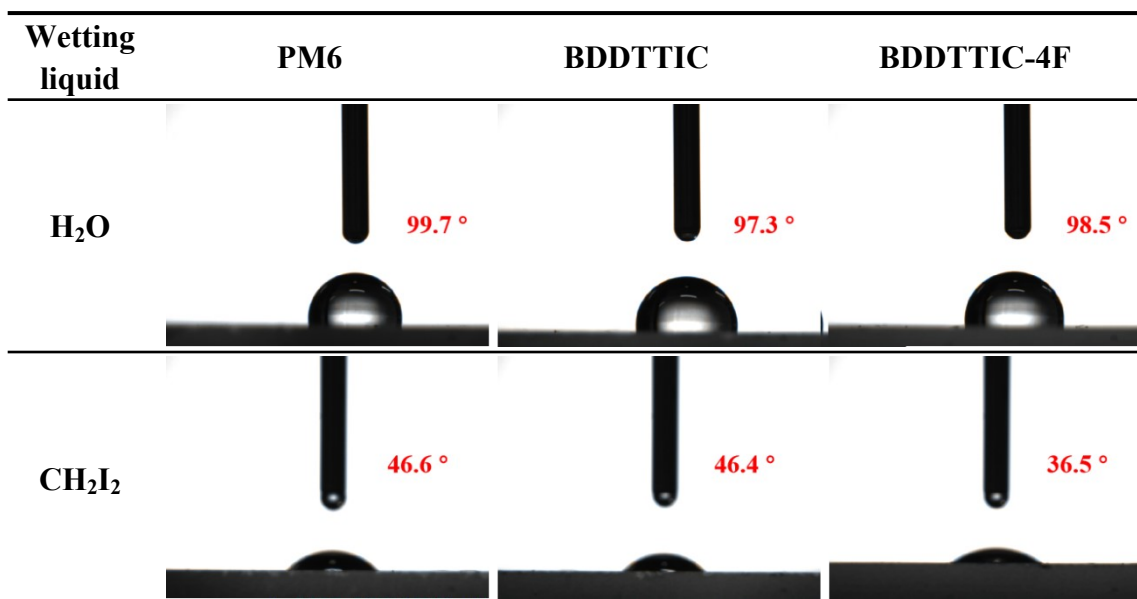


Figure S16. Views of surface contact measurements with the corresponding films.

Table S1. Photovoltaic properties of the BDDTTIC based OSCs with different polymer donors.

Donor	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]
J71	0.91	3.59	32.70	1.07
PTB7-Th	0.79	3.68	49.20	1.43
PBDB-T	0.86	5.93	40.46	2.06
PM6	0.95	7.05	44.84	3.00

D : A weight ratio is 1:1

Table S2. Photovoltaic properties of OSCs based on the PM6:BDDTTIC and PM6:BDDTTIC-4F blend films with different D/A ratios.

Blend films	D/A	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)
PM6:BDDTTIC	1:1.5	0.95	9.10	42.37	3.68
	1:2.0	0.95	8.93	44.00	3.72
	1:2.5	0.95	8.33	45.79	3.61
PM6:BDDTTIC-4F	1:1.5	0.75	8.15	41.40	2.54
	1:2.0	0.78	7.28	51.54	2.92
	1:2.5	0.79	7.49	48.37	2.87

Table S3. Photovoltaic properties of OSCs based on the PM6:BDDTTIC and PM6:BDDTTIC-4F blend films at different 1-chloronaphthalene ratio.

Blend films	1-Chloronaphthalene ratio	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
PM6:BDDTTIC	None	0.95	8.93	44.00	3.72
	0.50%	0.95	9.31	61.95	5.48
	0.75%	0.95	9.47	62.44	5.62
	1.00%	0.94	8.46	62.03	4.93
PM6:BDDTTIC-4F	None	0.78	7.28	51.54	2.92
	0.50%	0.72	5.49	49.26	1.95
	0.75%	0.70	5.95	44.57	1.86
	1.00%	0.67	5.54	41.38	1.54

Table S4. The contact angle and surface energy parameters of the PM6, BDDTTIC and BDDTTIC-4F films.

Surface	$\theta_{\text{H}_2\text{O}}$ ($^\circ$)	$\theta_{\text{CH}_2\text{I}_2}$ ($^\circ$)	γ^d (mNm^{-1}) ^a	γ^p (mNm^{-1}) ^a	γ (mNm^{-1}) ^a
PM6	99.7	46.6	36.9	0.07	37.00
BDDTTIC	97.3	46.4	35.8	0.29	36.00
BDDTTIC-4F	98.5	36.5	43.4	0	43.40

^a γ^d and γ^p represent the surface free energies generated from the dispersion forces and the polar forces, respectively