SUPPLEMENTARY INFORMATION

Efficient Non-fused Electron Acceptor with C-shaped Molecular Geometry for Photovoltaic Application

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Measurements and Instruments

^{1}H NMR spectra were recorded on a Bruker AVANCE 300 MHz NMR spectrometer at room temperature. The absorption spectra of the molecules in solution and in solid thin films were measured on a Hitachi UH3100 UV-vis spectrophotometer. The thickness of blend layers were measured via the surface profilometer Bruker Dektak XT. The AFM images were recorded using a Nanoscope V AFM in tapping mode. The *J–V* curves were measured under AM1.5G illumination, 100 mW cm^{-2} based on a class A+A+A+ solar simulator (Enlitech SS-X50). The light intensity was calibrated by the standard silicon solar cell. The EQE data were obtained using a solar cell spectral response measurement system (QE-R3011, Enlitech Technology Co., Ltd). The film thickness data were obtained via a surface profilometer (Dektak XT, Bruker). Photo-carrier extraction by linearly increasing voltage (Photo-CELIV) measurement was conducted using the Fluxim AG Paios all-in-one characterization platform. Sensitive FTPS-EQE (s-EQE) spectra were recorded using the Enlitech PECT-600 integrated system. Electroluminescence quantum efficiency (EQE$_{EL}$) and EL spectra were measured using a device (Enlitech ELCT-3010). The molecular energy levels were measured by utilizing CHI650D Electrochemical Workstation via square wave voltammetry methods. The working electrode, counter electrode, and reference electrode were Glassy carbon disk, Pt wire, and an Ag/Ag+ electrode respectively with the ferrocene/ferrocenium (Fc/Fc$^+$) as an external standard in the measurement. HOMO/LUMO= -e (φox/φred + 4.8-φFc/Fc$^+$) (eV).

DFT calculation

The molecular geometries were optimized by Gaussian 09 with a functional of B3LYP and a basis set of 6-31G (d, p). The long alkyl chains were replaced by methyl for saving computation time. The ESP analysis was carried out by a wavefunction analysis tool Multiwfn.[1]

Device fabrication

OSCs fabricated with a conventional structure of ITO/PEDOT:PSS/PBQx-TF:Acceptor/PFN-Br/Al. The ITO-coated glass was washed with deionized water/detergent, deionized water, acetone and ethanol in sequence for 15 minutes. Later, the ITO-coated glass was treated under the ultraviolet-ozone condition for 20 min. After that, PEDOT:PSS (Heraeus Clevios™ AI 4083) was spin coated onto the glass at 3000 r.p.m for 40 s and processed by thermal annealing at 160 °C for 15 min. To make PBQx-TF dissolved fully, the blends of PBQx-TF:Acceptor (1:1, w/w) was dissolved in toluene (Tol) at a total concentration of 5 mg mL^{-1} and stirred for 2 hours at 100 °C. Next, adding 0.5% (v/v) 1-Chloronaphthalene (CN) as additive into the host solution Tol prior to the spin-coating treatment. Afterwards, the blend solution was spin-coated and thermal annealed at 100 °C for 10 min. Subsequently, PFN-Br was spin-coated on the active layer at 3000 rpm for 30 s. Finally, the OSC was finished by evaporating 100 nm thick Al under high vacuum (about 2×10^{-4} Pa), resulting in a defined active area of 0.037 cm^2.

The control material OSCs fabricated with a conventional structure of ITO/PEDOT:PSS/PBQx-TF:A4T-16 /PDINN/Ag. The preparation process is as above, with the difference that the device uses 0.5% (v/v) 1,8-Diiodooctane (DIO) as an additive.

The preparation of single-crystal

A solution of approximately 1 mg of AC2 in ~0.5 mL of chloroform was prepared and transferred into a 4 mL volumetric flask, which was then sealed with a cap. The 4 mL volumetric flask was subsequently placed inside a 20 mL vial containing approximately ~3 mL of petroleum ether (PE). The 20 mL volumetric flask was sealed and left undisturbed for 5-7 days, allowing the formation of rod-shaped clusters. The crystallographic parameters are summarized in **Table. S7**. The CCDC number of AC2 is 2414348.

Materials and Synthesis.

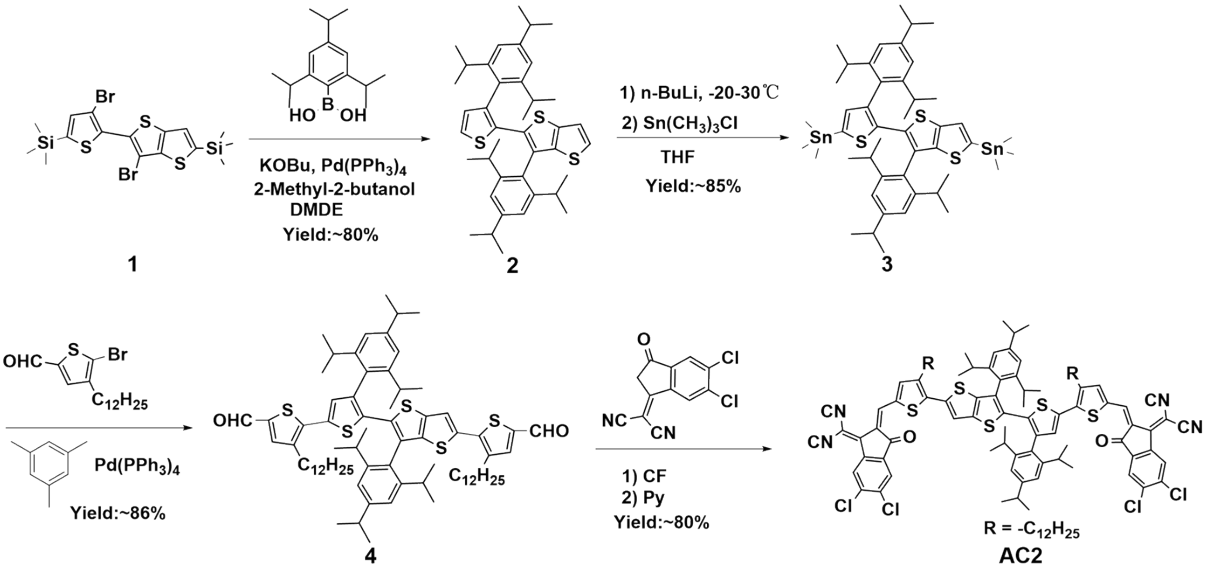


Fig. S1. The detailed synthetic route of AC2 molecule.

Compound 1, PBQx-TF, A4T-16, PFN-Br, 5,6-dichloride-3(dicyanomethylidene)indan-1-one and 5-bromo-4-dodecyl thiophene-2-carbaldehyde were purchased from Solarmer Materials Inc. 2,4,6triisopropylphenylboronic acid were purchased from Innochem. PEDOT: PSS, Clevios™ P VP AI 4083, was purchased from Heraeus. The other reagents and solvents were commercially available and used as received.

3-(2,4,6-triisopropylphenyl)-2-(3-(2,4,6-triisopropylphenyl)thiophen-2-yl)thieno[3,2-b]thiophene (compound 2)

Compound 2 was obtained by Suzuki coupling according to the previous literature,[2] and the detailed synthesis procedure is as follows. Compound 1 (2.5 g, 4.79 mmol), 2,4,6-triisopropylphenylboronic acid (4.75 g, 19.16 mmol) and $Pd(PPh_3)_4$ (600 mg, 0.48 mmol) was dissolved in 80 mL of Diethylene glycol dimethyl ether (DMDE) in a 250 mL flask under inert atmosphere. Then, a solution of KOBu (3.76 g, 33.5 mmol) in 2-Methyl-2-butanol (20 mL) was added into the flask via syringe. The mixture was stirred and refluxed for 48 hours under argon protection in 120 °C. After cooling the reactant to room temperature, a mixed solution of H_2O (10 mL) and methanol (50 mL) was added, and the raw product can be precipitated and filtered. The product was purified by recrystallization from isopropanol and obtained as white solid powder with a yield of 80%.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.19 (d, *J* = 5.2 Hz, 1H), 7.13 (d, *J* = 7.3 Hz, 4H), 7.04

(dd, *J* = 6.1, 5.1 Hz, 2H), 6.69 (d, *J* = 5.1 Hz, 1H), 3.02 (p, *J* = 6.9 Hz, 2H), 2.64 (pd, *J* = 7.0, 5.4 Hz, 4H), 1.37 (d, *J* = 6.9 Hz, 12H), 1.13 – 1.01 (m, 24H).

trimethyl(4-(2,4,6-triisopropylphenyl)-5-(3-(2,4,6-triisopropylphenyl)-5-(trimethylstannyl)thieno[3,2-b]thiophen-2-yl)thiophen-2-yl)stannane (compound 3)

Compound 2 (1.0 g, 1.6 mmol), dry THF (30 mL), was added to 100 mL two-necked flask, dissolved for 30 min and protected by argon. The reaction mixture was cooled to -20 to -30 °C in an acetonitrile bath, and n-butyllithium (n-BuLi, 2.5 M, 4 mmol) was slowly added over 10 min under low-temperature conditions. After being removed from the cold bath, the mixture was stirred for 30 min, during which a large amount of solid appeared. Then, Me_3SnCl (1.0 M, 5.59 mmol) was added at room temperature, and the solution immediately became clear. The reaction was allowed to proceed for 30 min and then washed with water and extracted with dichloromethane (DCM). The product was recrystallized using 30 mL of isopropanol to obtain 1.1 g white crystals with a yield of 85%.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.13 (s, 1H), 7.10 (s, 4H), 6.71 (s, 1H), 3.05 – 2.99 (m, 2H), 2.66 – 2.60 (m, 5H), 1.37 (q, *J* = 2.2 Hz, 12H), 1.07 – 1.02 (m, 24H), 0.31 (s, 9H), 0.19 (s, 9H).

3-dodecyl-5'-(5-(3-dodecyl-5-formylthiophen-2-yl)-3-(2,4,6-triisopropylphenyl)thieno[3,2-b]thiophen-2-yl)-4'-(2,4,6-triisopropylphenyl)-[2,2'-bithiophene]-5-carbaldehyde (compound 4)

Compound 3 (1 g, 1.05 mmol), trimethylbenzene (10 mL), 5-bromo-4-dodecyl thiophene-2-carbaldehyde (1.32 g, 3.68 mmol), and the catalyst $Pd(PPh_3)_4$ (60 mg) were added to a 25 mL two-necked flask under argon protection. The reaction was carried out in an oil bath at 120°C for 12 h. After the reaction was complete, the mixture was directly spun-dried over the silica gel column (100-200 mesh). A mixture of petroleum ether: dichloromethane (PE:DCM, v:v=1:1) was used to remove impurities, followed by a mixture of PE:DCM (v:v=1:2) to elute 1.07 g of pure product with a yield of 86%.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 9.79 (d, *J* = 5.3 Hz, 2H), 7.55 (d, *J* = 12.9 Hz, 2H), 7.31 (s, 1H), 7.21 (d, *J* = 12.3 Hz, 4H), 7.00 (s, 1H), 3.07 (p, *J* = 6.9 Hz, 2H), 2.78 (t, *J* = 7.8 Hz, 2H), 2.70 (dt, *J* = 13.4, 6.8 Hz, 4H), 2.59 (t, *J* = 7.4 Hz, 2H), 1.41 (dd, *J* = 6.9, 2.1 Hz, 12H), 1.29 (s, 40H), 1.18 – 1.09 (m, 24H), 0.90 (t, *J* = 6.6 Hz, 6H).

2-((1Z,2Z)-5,6-dichloro-2-((5'-(5-(5-(((Z)-5,6-dichloro-1-(diisocyanomethylene)-3-oxo-1,3-dihydro-2H-inden-2-ylidene)methyl)-3-dodecylthiophen-2-yl)-3-(2,4,6-triisopropylphenyl)thieno[3,2-b]thiophen-2-yl)-3-dodecyl-4'-(2,4,6-triisopropylphenyl)-[2,2'-bithiophen]-5-yl)methylene)-3-oxo-2,3-dihydro-1H-inden-1-ylidene)-2-isocyanoacetonitrile (AC2)

Compound 4 (0.28 g, 0.24 mmol) and 5,6-dichloride-3(dicyanomethylidene)indan-1-one (0.31 g, 1.18 mmol) were dissolved in chloroform (5 mL). Pyridine (0.2 mL) was added and the reaction mixture was stirred at 45 °C for 2 hours. The mixture was directly spun-dried over the silica gel column (200-300 mesh). A mixture of PE:DCM (v:v=1:1) was used to remove impurities, followed by a mixture of PE:DCM (v:v=4:5) to elute 321.4 mg of solid product with a yield of 80%.

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.78 – 8.68 (m, 4H), 7.90 (d, *J* = 1.3 Hz, 2H), 7.60 (d, *J* = 7.0 Hz, 2H), 7.54 (s, 1H), 7.31 (s, 1H), 7.25 (s, 2H), 7.20 (s, 2H), 3.08 (p, *J* = 6.9 Hz, 2H), 2.79 (t, *J* = 7.8 Hz, 2H), 2.67 (dp, *J* = 9.6, 6.7 Hz, 4H), 2.55 (t, *J* = 7.4 Hz, 2H), 1.66 (dq, *J* = 15.3, 7.8, 6.9 Hz, 2H), 1.42 (dd, *J* = 6.9, 1.9 Hz, 12H), 1.27 (dd, *J* = 10.8, 2.8 Hz, 38H), 1.14 (s, 24H), 0.92 – 0.85 (m, 6H).

^{13}C NMR (175 MHz, Chloroform-*d*) δ 158.20, 158.08, 151.03, 150.68, 150.57, 150.12, 148.77, 148.10, 147.75, 141.48, 141.38, 139.67, 139.58, 139.36, 139.18, 138.62, 137.82, 137.76, 137.07, 136.94, 136.81, 135.96, 134.54, 134.40, 133.84, 131.80, 130.75, 129.61, 127.84, 126.89, 125.17, 125.12, 122.46, 121.78, 121.36, 121.13, 114.27, 114.20, 34.52, 34.50, 31.94, 31.16, 30.93, 29.85, 29.75, 29.69, 29.67, 29.65, 29.63, 29.62, 29.60, 29.59, 29.55, 29.43, 29.42, 29.38, 29.36, 25.63, 25.23, 24.28, 24.19, 23.96, 23.38, 22.71, 14.14.

MS (MALDI-TOF): m/z 1673.56490

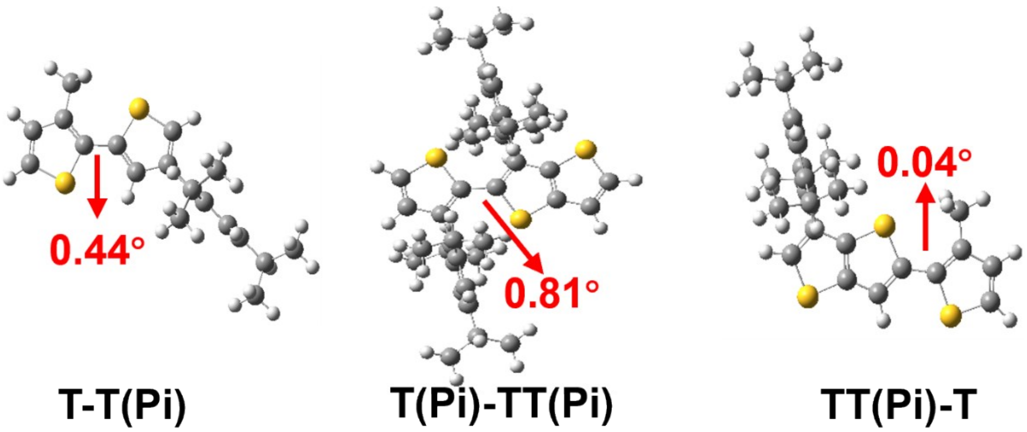


Fig. S2. The dihedral angles of the optimized structural units T-TT(P*i*), TT(P*i*)-T(P*i*) and T(P*i*)-T were calculated by DFT at the B3LYP/6-31G (d, p) level.

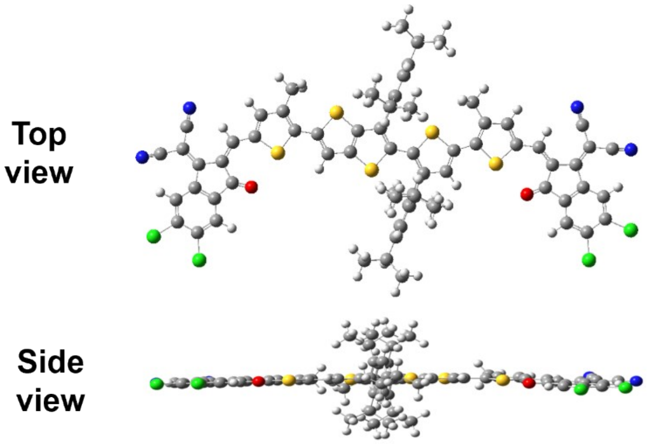


Fig. S3. The top view and side view of AC2 by DFT calculation.

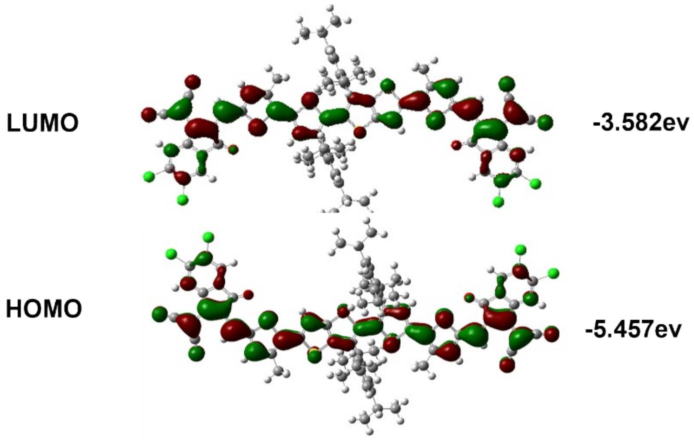


Fig. S4. Optimized geometries and distribution patterns of HOMO/LUMO of simplified AC2 molecule at B3LYP/6-31G (d, p) level.

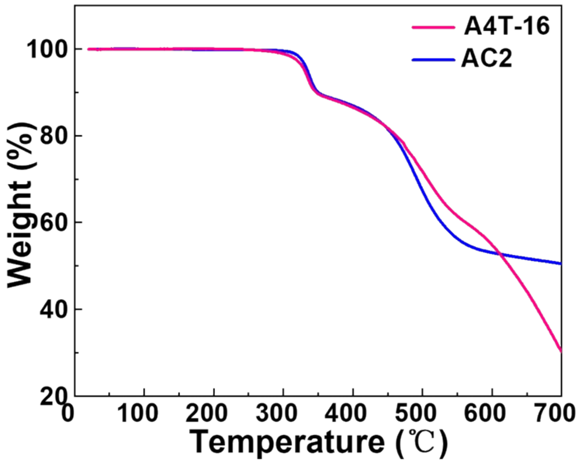


Fig. S5. TGA curve for AC2 and A4T-16 measured under nitrogen atmosphere at a heating rate of 10 °C min^{-1}.

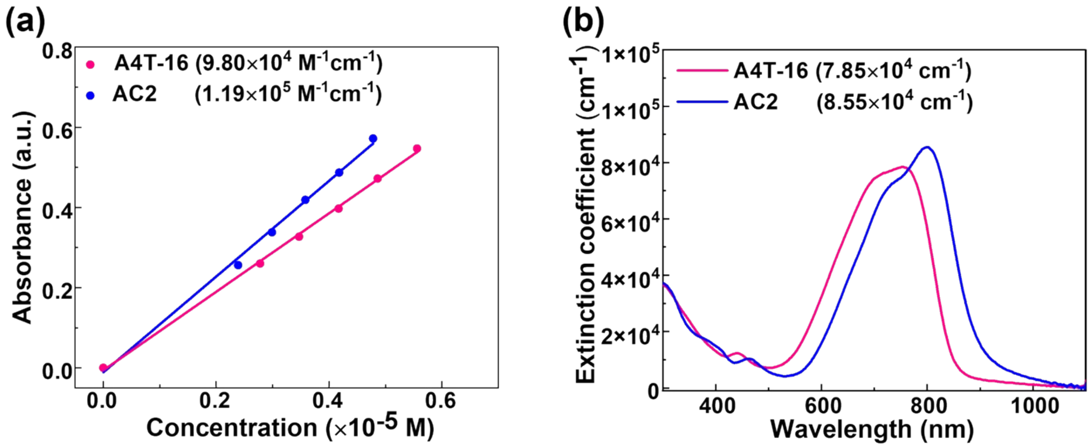
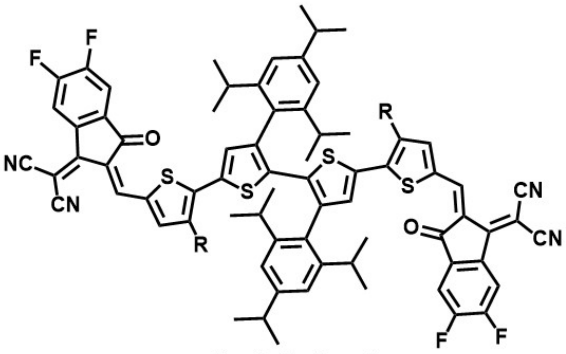


Fig. S6. The molar extinction coefficients of the two NFAs (a) in chloroform solution and (b) in solid state.



R = 2-ethylhexyl

A4T-16

Fig. S7. Chemical structures of A4T-16.

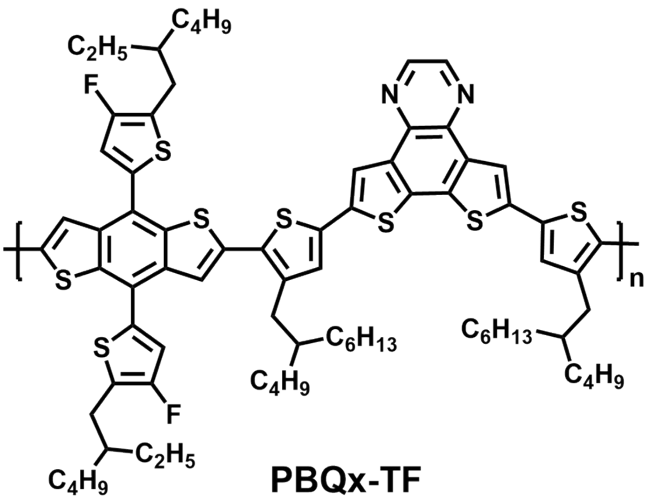


Fig. S8. Chemical structures of PBQx-TF.

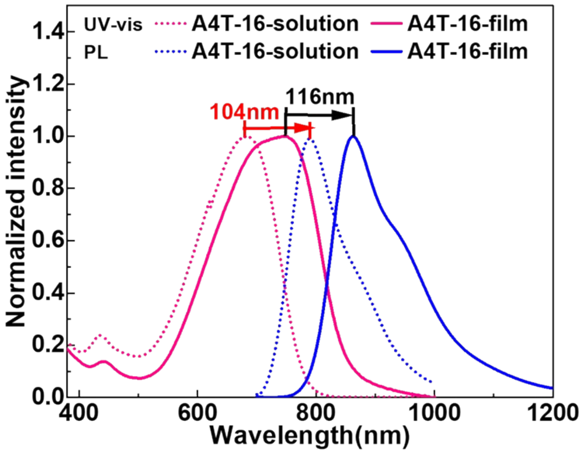


Fig. S9. Normalized absorption and PL spectra of A4T-16 in solution and film.

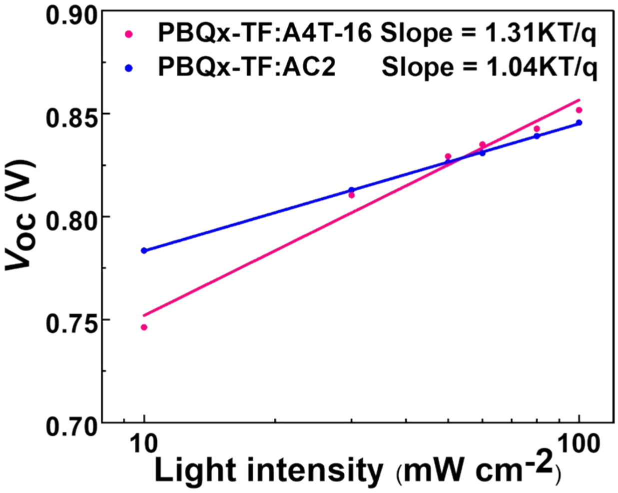


Fig. S10. The light-intensity (P_{light}) dependence of V_{OC}.

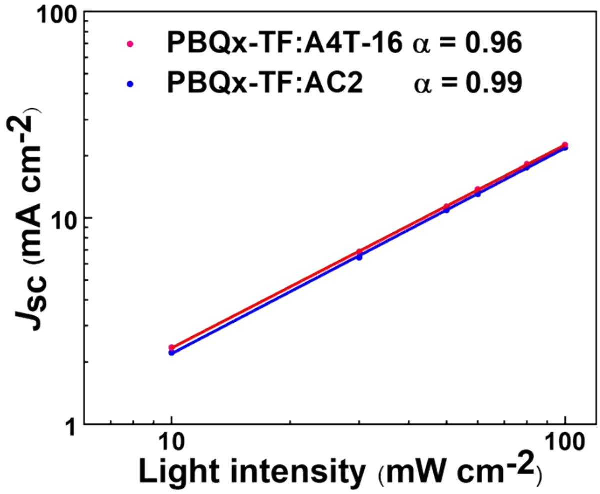


Fig. S11. The light-intensity (P_{light}) dependence of J_{SC}.

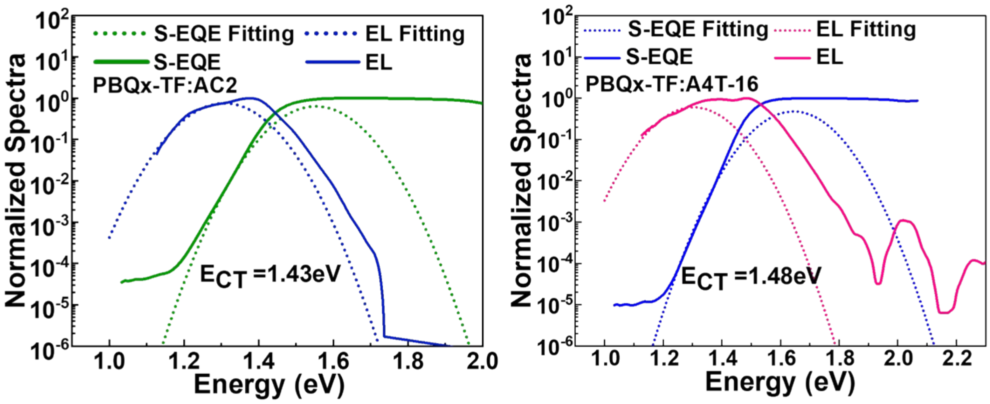


Fig. S12. Normalized EL and s-EQE spectra along with their corresponding fitting curve of PBQx-TF:AC2 and PBQx-TF:A4T-16.

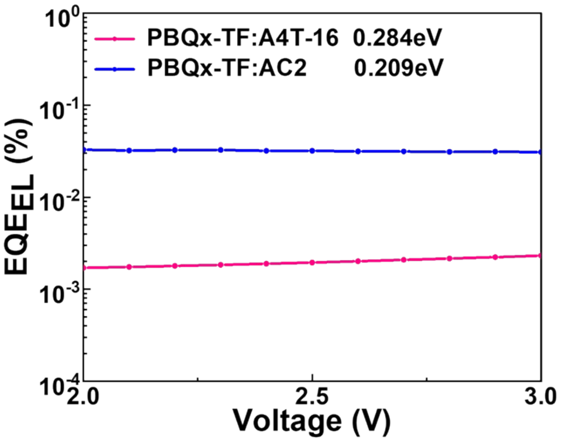


Fig. S13. The EQE_{EL} curve of PBQx-TF:AC2 and PBQx-TF:A4T-16.

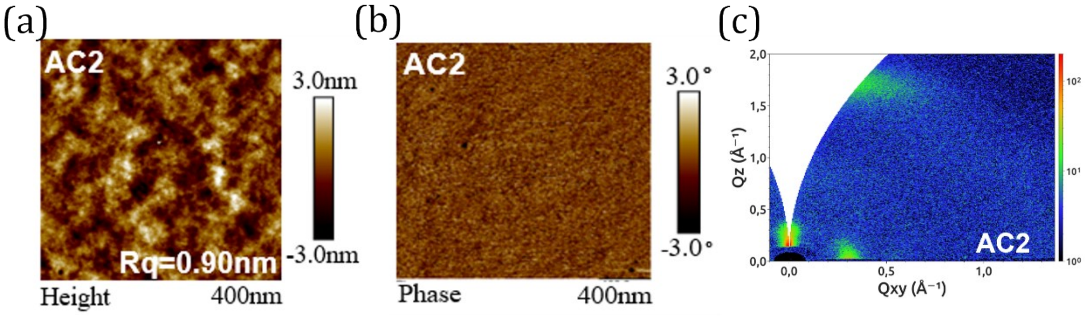


Fig. S14. (a-b) The AFM height and phase images and (c) the GIWAXS pattern of AC2 pure film.

Table. S1. Optical and electrochemical properties of the studied NFAs.

NFAs	λ_{max}^{sol} [nm]	λ_{max}^{film} [nm]	λ_{onset}^{sol} [nm]	λ_{onset}^{film} [nm]	E_g^{opt} [eV]	E_{HOMO} [eV]	E_{LUMO} [eV]
AC2	729	801	815	905	1.37	-5.66	-4.04
A4T-16	686	754	723	850	1.46	-5.71	-4.02

Table. S2. The devices optimization based on ITO/PEDOT:PSS/PBQx-TF:AC2/PFN-Br/Al by different solvents.

Solvents	V_{OC} [V]	J_{SC} [mA/cm^2]	FF [%]	PCE [%]
Tol	0.857	23.12	62.90	12.46
DMB	0.856	22.46	64.80	12.46
CF	0.860	19.02	38.00	6.21
CB	0.869	20.35	44.20	7.81

Table. S3. The devices optimization based on ITO/PEDOT:PSS/ PBQx-TF:AC2/PFN-Br/Al by D/A ratios.

D:A ratio	V_{OC} [V]	J_{SC} [mA/cm^2]	FF [%]	PCE [%]
1:0.5	0.871	14.41	65.70	8.25
	0.880	18.32	64.10	10.33
1:1	0.870	22.88	66.36	13.21

01:1.5	0.875	23.02	63.80	12.85
	0.859	22.51	54.40	10.53
	0.865	22.42	44.30	8.60

Table. S4. The devices optimization based on ITO/PEDOT:PSS/ PBQx-TF:AC2/PFN-Br/Al by different additives with toluene as the host solvents.

Additive	V_{OC} [V]	J_{SC} [mA/cm^2]	FF [%]	PCE [%]
0.5%CN	0.850	23.00	68.18	13.33
0.5%DIO	0.855	23.00	57.10	11.22
0.5%NMP	0.853	21.94	49.00	9.18
0.5%DPE	0.853	23.01	64.30	12.62

Table. S5. The devices optimization based on ITO/PEDOT:PSS/ PBQx-TF:AC2/PFN-Br/Al by different annealing conditions.

Annealing condition	V_{OC} [V]	J_{SC} [mA/cm^2]	FF [%]	PCE [%]
none	0.869	22.50	63.00	12.32
60℃,10 min	0.865	22.55	64.60	12.59
80℃,10 min	0.862	22.43	63.70	12.31
100℃,10 min	0.860	23.82	69.00	14.21
120℃,10 min	0.832	23.69	52.80	10.41

Table. S6. Detailed parameters of the GIWAXS.

Samples	In-plane (100)				Out-of-plane (010)			
	$q_{x\text{-}y}$ [Å^{-1}]	d [Å]	FWHM [Å^{-1}]	L_c [Å]	q_z [Å^{-1}]	d [Å]	FWHM [Å^{-1}]	L_c [Å]
AC2	0.339	18.53	0.097	58.27	1.739	3.611	0.286	19.762
PBQx-TF: A4T-16	0.346	18.15	0.096	59.50	1.771	3.546	0.376	15.032
PBQx-TF: AC2	0.323	19.44	0.097	58.50	1.761	3.566	0.227	24.898

Table. S7. The crystallographic data of AC2.

Empirical formula	$C_{168}H_{140}Cl_8N_8O_4S_{10}$
Formula weight	2939.07

Temperature/K	169.99(12)
Crystal system	trigonal
Space group	R32
a/Å	58.5699(5)
b/Å	58.5699(5)
c/Å	36.0135(4)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	106990(2)
Z	18
ρ_{calc}g/cm^3	0.821
μ/mm^{-1}	1.975
F(000)	27576.0
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	3.008 to 151.564
Index ranges	$-73 \leq h \leq 71$, $-62 \leq k \leq 73$, $-44 \leq l \leq 44$
Reflections collected	253050
Independent reflections	47209 [R_{int}= 0.0759, R_{sigma}= 0.0398]
Data/restraints/parameters	47209/271/1806
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1= 0.0827, wR_2= 0.2290
Final R indexes [all data]	R_1= 0.1313, wR_2= 0.2894
Largest diff. peak/hole / e Å^{-3}	0.60/-0.38
Flack parameter	0.495(6)

SUPPLEMENTARY NMR FIGURES

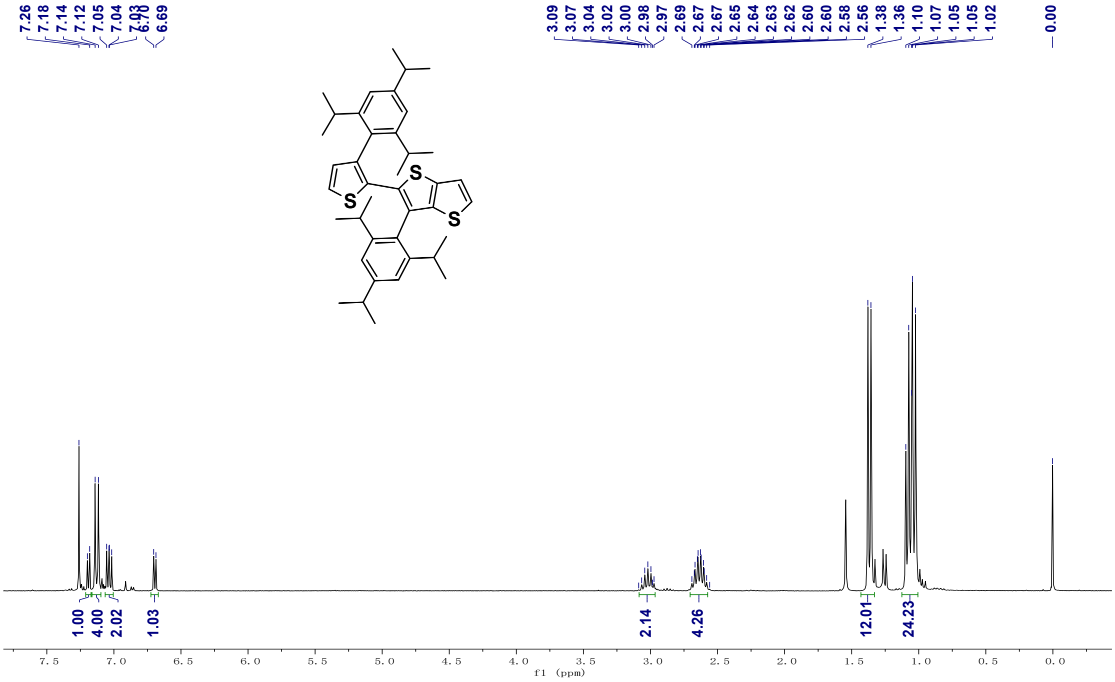


Fig. S15. ^{1}H NMR spectrum of compound 2 of AC2.

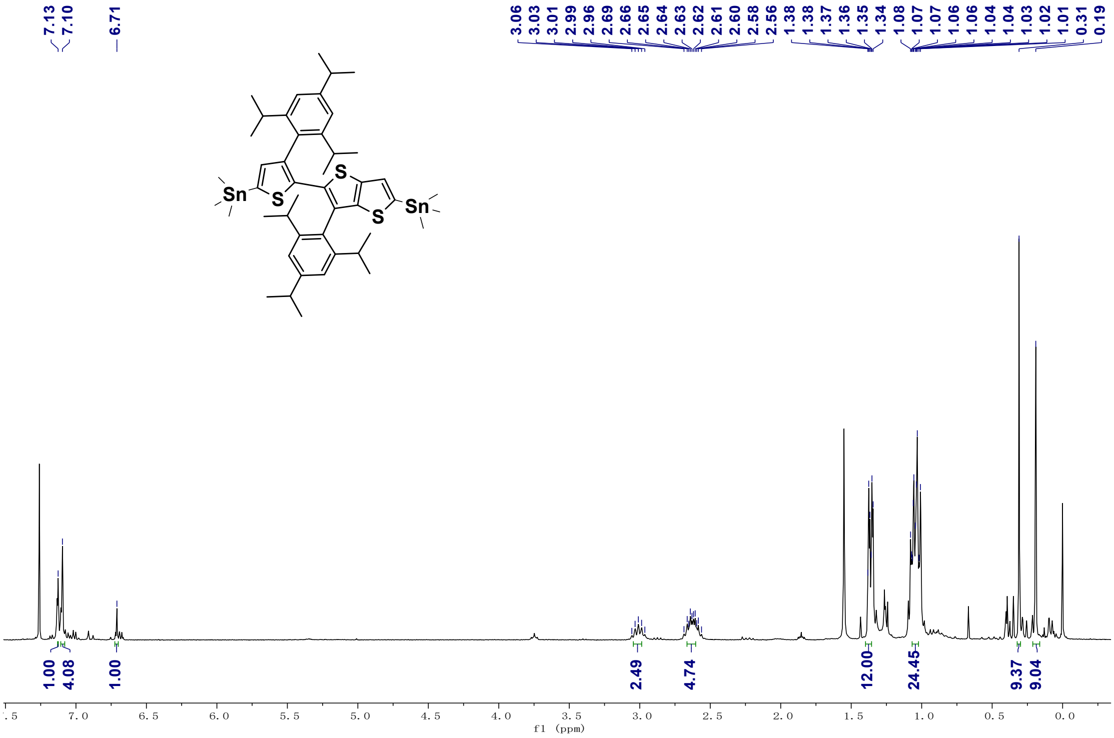


Fig. S16. ^{1}H NMR spectrum of compound 3 of AC2.

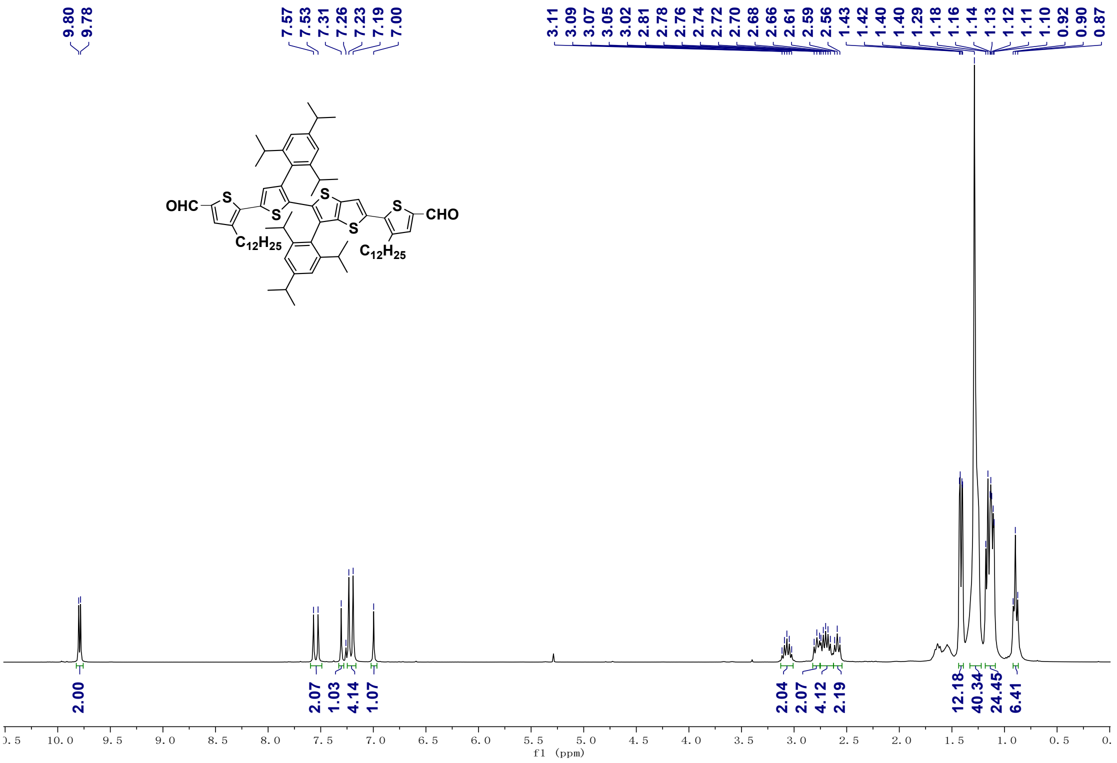


Fig. S17. ^{1}H NMR spectrum of compound 4 of AC2.

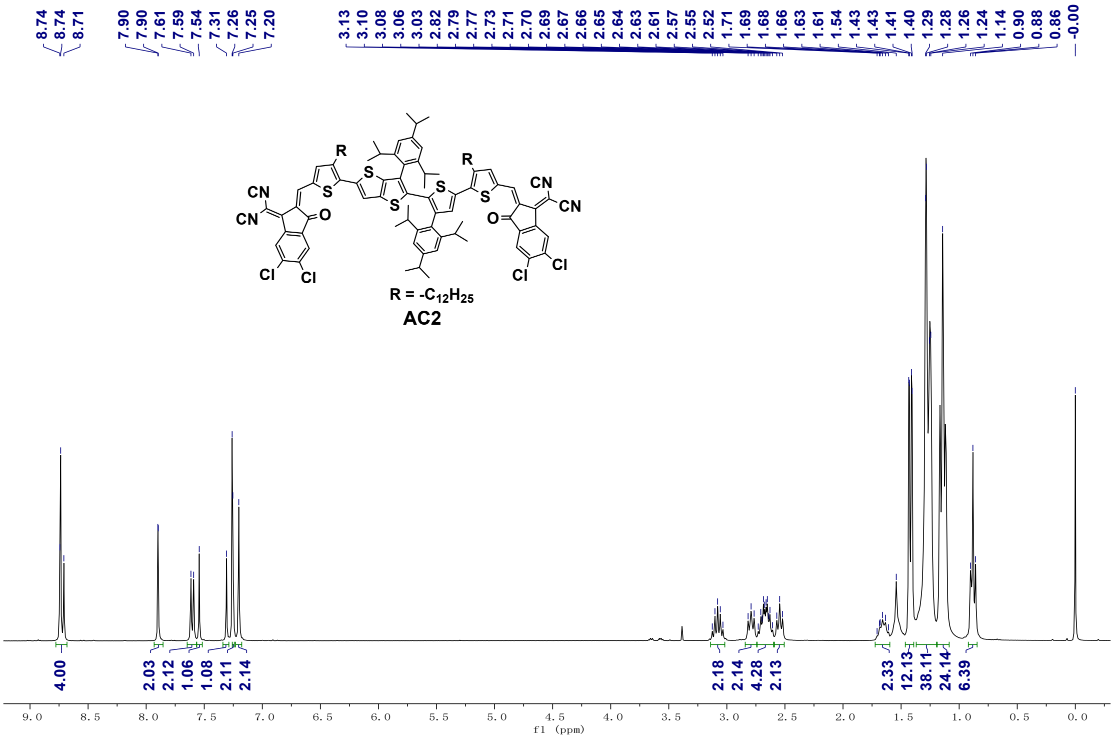


Fig. S18. ^{1}H NMR spectrum of AC2.

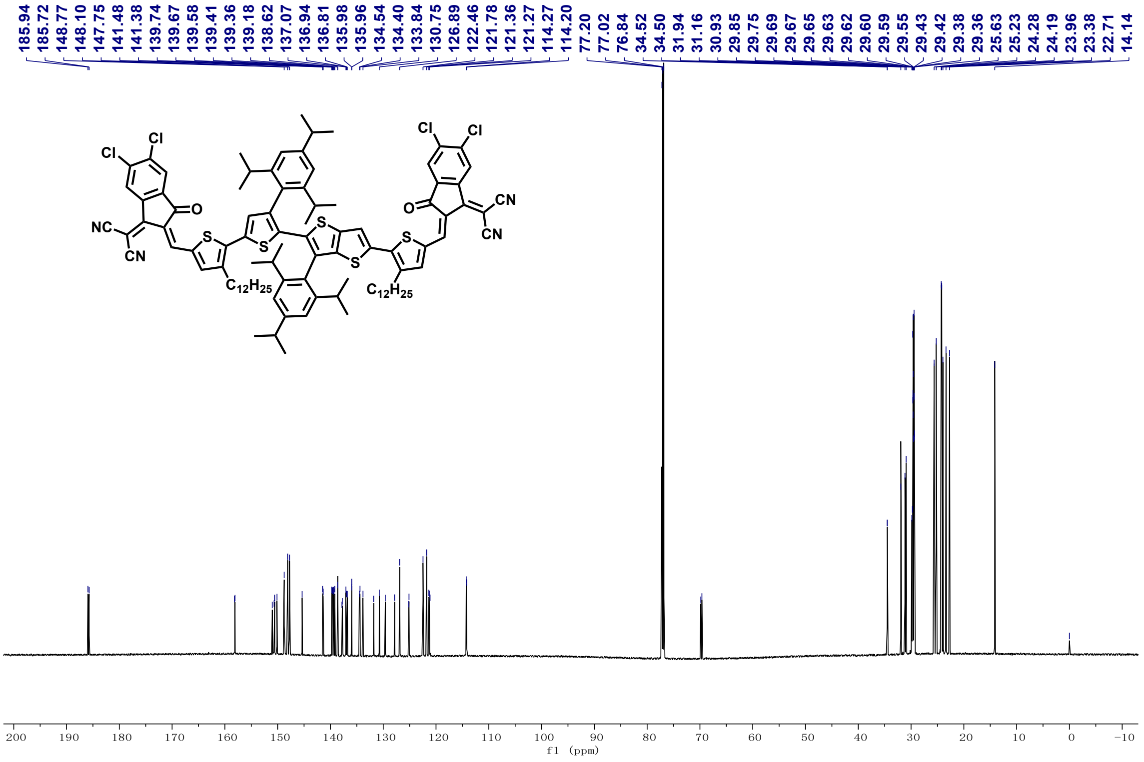


Fig. S19. ^{13}C NMR spectrum of AC2.

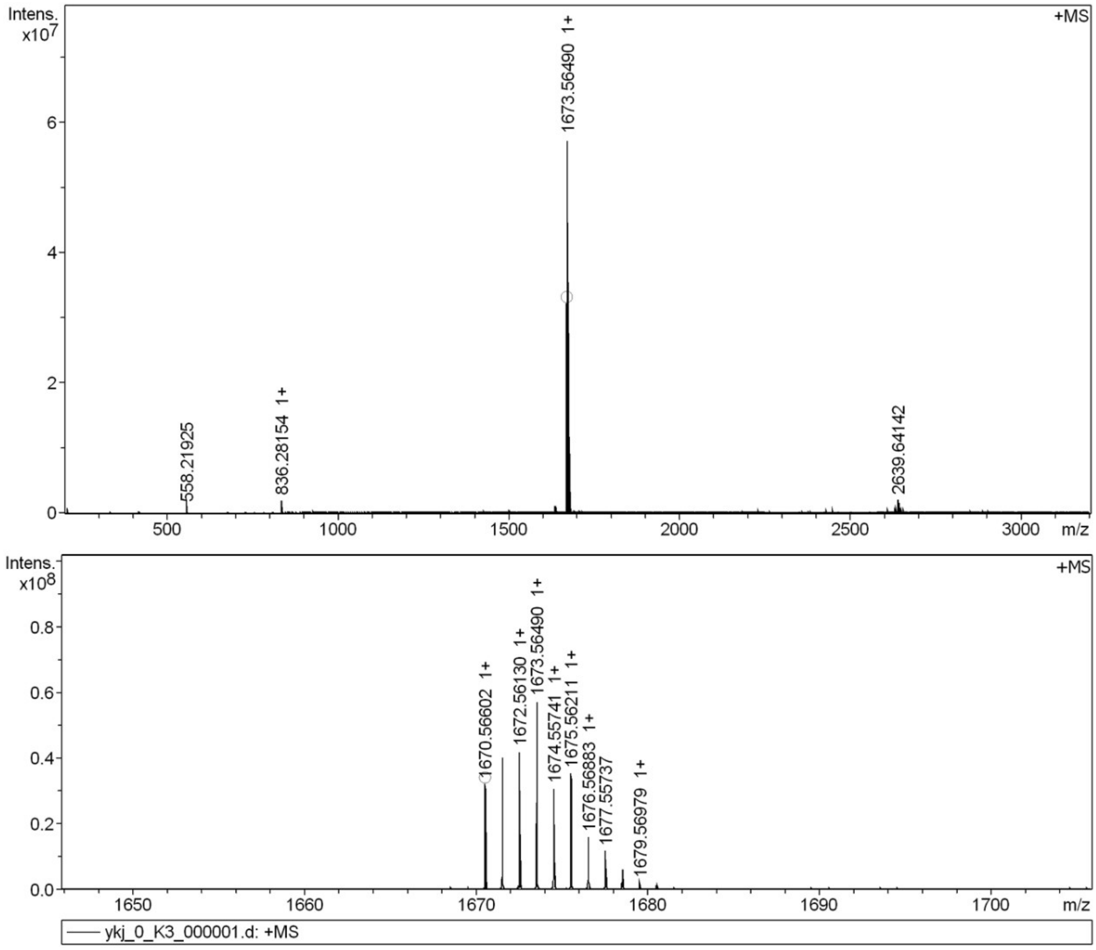


Fig. S20. MS (MALDI-TOF) spectrum of AC2.

References

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(2) Organ, M. G.; Çalimsiz, S.; Sayah, M.; Hoi, K. H.; Lough, A. J. Pd-PEPPSI-IPent: An Active, Sterically Demanding Cross-Coupling Catalyst and Its Application in the Synthesis of Tetra- *Ortho* -Substituted Biaryls. *Angew. Chem., Int. Ed.,* **2009**, *48* (13), 2383–2387.