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Supporting Information

Development of Degradable Networked-Organic Semiconductors and Effects on Charge Carrier Mobility in Organic Thin-Film Transistors

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1. Materials

Unless stated otherwise, all of the chemicals were purchased from Aldrich and used without further purification. BTR-Cl and L8-BO was purchased from Derthon and 1-Material, respectively. Compound Y5-Br[1] and PO-N[2-4] were synthesized according to the procedure reported in the literature.

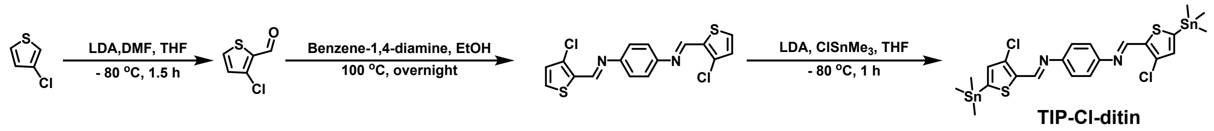
2. Characterizations

The UV–Vis absorption spectra were measured from Lambda 365 UV/VIS Spectrometer (PerkinElmer). The Fourier-transform infrared spectroscopy (FT-IR) spectra were obtained from Spectrum 100 (PerkinElmer) using ATR mode. And the film samples for UV–Vis and FT-IR were prepared by spin coating in nitrogen-filled gloves box with 10 mg/mL solution in chloroform (CF). The atomic force microscopy (AFM) images of the films were obtained using a Park Systems AFM (XE-100) in non-contact mode. The gel-permission chromatography of degradable polymer formed at a film state was performed to obtain the molecular weight and polymerization yield. The polymerization yield through GPC is estimated by comparing the number of repeating units in the broad polymer peak, unreacted monomer peak, and their area ratio.

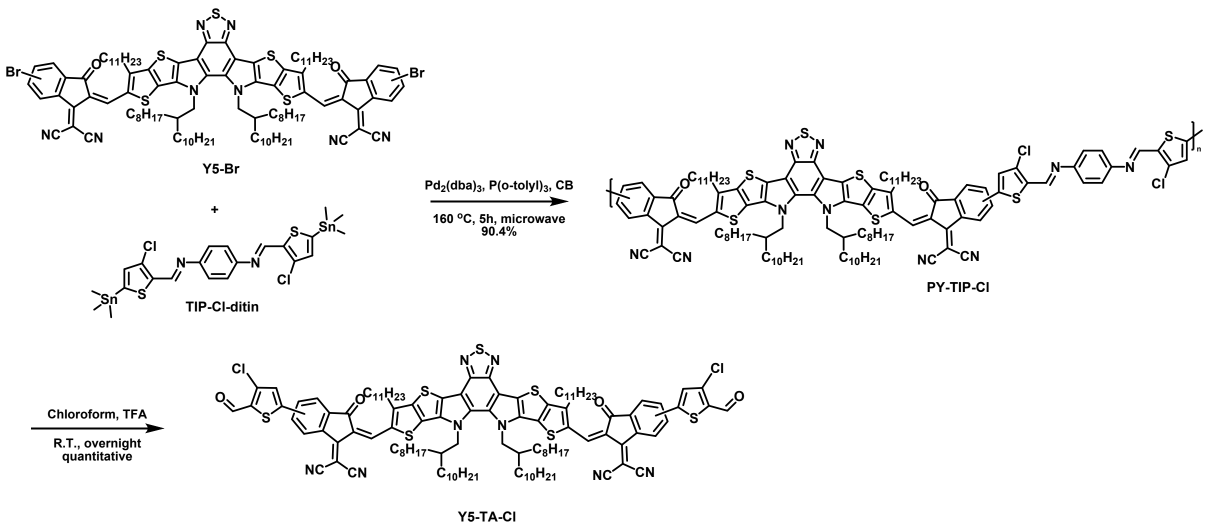
The synthesized monomer was characterized by measuring ^{1}H and ^{13}C nuclear magnetic resonance spectroscopy (NMR) spectra using a Bruker 400 MHz NMR spectrometer in $CDCl_3$.

Grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements were performed at the 9A U-SAXS beamline of Pohang Light Source-II (PLS-II) with an X-ray wavelength of 1.12 Å. 2D scattering patterns were recorded with a 2D charge coupled detector (CCD) (Rayonix Ltd., MX170-HS).

3. Synthesis of monomer and polymer



Scheme S1 Synthetic route of TIP-Cl-ditin.



Scheme S2 Synthetic route of Y5-TA-Cl.

Synthesis of 3-chlorothiophene-2-carbaldehyde

3-Chlorothiophene (1.0 g, 8.4 mmol) was dissolved in dry tetrahydrofuran (THF, 14 mL) under Argon (Ar) gas. The solution was cooling to –80 °C and lithium diisopropylamide (9.3 mL, 9.3 mmol, 1 M in hexane) was added slowly dropwise into the reaction flask at –80 °C for 90 min. Anhydrous *N,N*-dimethylformamide (0.7 mL, 9.3 mmol) was added dropwise to the reaction flask. After the 10 min, the reaction flask was transferred to room temperature and overnight stirring. The reaction mixture was quenched with aqueous NH_4Cl solution and extracted twice with ether. The organic layer was dried over $MgSO_4$ and removed organic solvent (1.02 g, 82.5%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 10.06 (s, 1H), 7.72 (d, 2H), 7.07 (d, 2H).

Synthesis of TIP-Cl

Benzene-1,4-diamine (0.2 g, 1.85 mmol) and 3-chlorothiophene-2-carbaldehyde (1.08 g, 7.40 mmol) were dissolved in ethanol (18.5 mL) at room temperature. The reaction mixture was refluxed at 100 °C for overnight. After reaction, flask was cooling to room temperature and filtered with ethanol. The product was washed with ethanol and vacuum dry (0.59 g, 87.4%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.70 (s, 2H), 7.48 (d, 2H), 7.30 (s, 4H), 7.02 (d, 2H).

Synthesis of TIP-Cl-Sn

TIP-Cl (300 mg, 0.82 mmol) was dissolved in dry THF (8.2 mL) under Ar gas. The solution was cooling to –80 °C and lithium diisopropylamide (1.8 mL, 1.81 mmol, 1 M in hexane) was added slowly dropwise into the reaction flask at –80 °C for 1 h. Trimethyltin chloride (1.97 mL, 1.97 mmol, 1 M in hexane) was added reaction mixture and stirring for 30 min at –80 °C. After the 30 min, the reaction flask was transferred to room temperature and overnight stirring. The reaction mixture was work up with dichloromethane (DCM) and water. Removed the DCM, recrystallization with hexane. The product was dissolved in hexane (228.3 mg, 40.3%). ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 8.66 (s, 2H), 7.29 (s, 4H), 7.06 (s, 2H), 0.42 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ(ppm): 149.8, 149.6, 145.1, 139.8, 135.9, 130.6, 122.2, –8.2.

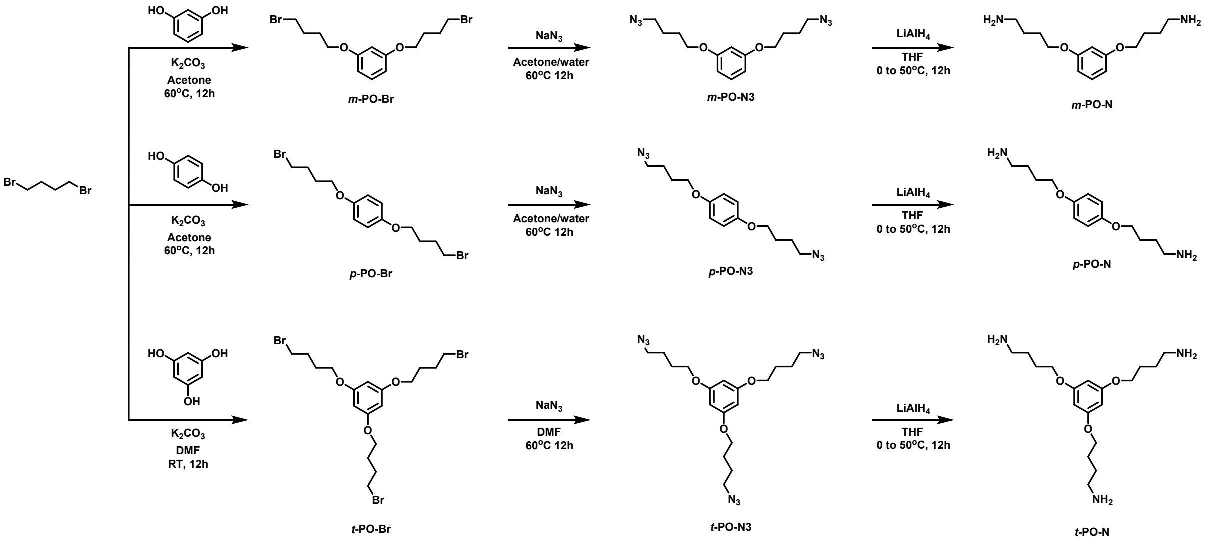
Synthesis of PY-TIP-Cl

Y5-Br (250 mg, 0.13 mmol), TIP-Cl-ditin (90 mg, 0.13 mmol), $Pd_2(dba)_3$ (2.4 mg, 2 mol%) and $P(o\text{-tolyl})_3$ (3.2 mg, 8 mol%) were dissolved in chlorobenzene (CB, 2.7 mL) under Ar gas. After purging by Ar gas for 20 min, the reaction mixture was heated under microwave conditions at 160 °C for 1 h. TIP-Cl-ditin (9 mg, 0.013 mmol) and CB (1 mL) added the microwave tube and purge with Ar gas for 15 min. The reaction mixture was heated under microwave conditions at 160 °C for 2 h. After the reaction, the crude polymer was precipitated into acetone and collected at a thimble filter. The polymer was purified by successive Soxhlet extraction with hexane and methanol. The CF fraction was concentrated by a rotary evaporator and precipitated in acetone. Finally, the precipitate was collected to obtain the polymer PY-TIP-Cl (82.5 mg, 31.6%).

Hydrolysis of PY-TIP-Cl and extracted of monomer Y5-TA-Cl

In a 250 mL of round bottom flask, polymer PY-TIP-Cl was dissolved into 130 mL of CF. 13 mL of trifluoroacetic acid (TFA) (1 M in deionized (DI) water) was added to the flask. The mixture was stirred overnight at room temperature. After the reaction, the organic layer was washed with DI water two times, dried with anhydrous $MgSO_4$. The crude material was concentrated under pressure and purified via column chromatography, giving of a blue solid (82.5 mg, 31.6%). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 10.11 (s, 0.65H), 10.02 (s, 0.82H), 9.18 (d, 2H), 8.93 (s, 0.88H), 8.78 (d, 0.63H), 8.13 (s, 0.56H), 8.01-7.96 (dd, 3.8H), 7.48 (s, 0.8H), 7.39 (s, 1.40H), 4.80 (d, 4.69H), 3.22 (br, 5.01H), 2.17 (br, 2.44H), 1.88 (br, 6.69H).

4. Synthesis of crosslinker PO-N



Scheme S3 Synthetic route of cross linkers PO-N.

Synthesis of PO-Br

Resorcinol (5 g, 45 mmol) and potassium carbonate (18.8 g, 14 mmol) were dissolved in acetone and stirred at 60 °C for 15 min. 1,4-Dibromobutane (21.7 mL, 18 mmol) was added to the reaction mixture and stirred at 60 °C for 12 h. After completion of the reaction, the solvent was removed under reduced pressure. The reaction mixture was poured into water, and then extracted with CF. The combined organic layer was dried over $MgSO_4$, and evaporated under reduced pressure. The residue was purified with column chromatography on silica gel using ethyl acetate/hexane (1/9, v/v) as the eluent to afford ***m*-PO-Br** (13.8 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.28-7.14 (t, 1H), 6.49-6.44 (m, 3H), 3.99-3.96 (t, 4H), 3.50-3.47 (t, 4H), 2.08-1.92 (t, 8H).

***p*-PO-Br:** *p*-PO-Br was synthesized according to the similar procedure to that for *m*-PO-Br with hydroquinone (5 g, 45 mmol), potassium carbonate (18.8 g, 14 mmol) and 1,4-dibromobutane (21.7 mL, 18 mmol) (12.6 g, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.81 (s, 4H), 3.98-3.92 (t, 4H), 3.38-3.34 (t, 4H), 2.17-1.77 (m, 8H).

***t*-PO-Br:** *t*-PO-Br was synthesized according to the similar procedure to that for *m*-PO-Br with phloroglucinol (5 g, 0.039 mol), potassium carbonate (27.3 g, 20 mmol) and 1,4-dibromobutane

(28.4 mL, 24 mmol) (10.8 g, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.81 (s, 3H), 3.96-3.93 (t, 6H), 3.50-3.47 (t, 6H), 2.07-1.92 (m, 12H).

Synthesis of PO-N3

m-PO-Br (8.9 g, 23 mmol) and sodium azide (4.6 g, 70 mmol) were dissolved in a mixture of acetone/water (4:1, 200 mL) and the reaction mixture and stirred at 60 °C for 12 h. After completion of the reaction, the solvent was removed under reduced pressure. The reaction mixture was poured into water, and then extracted with CF. The combined organic layer was dried over $MgSO_4$, and evaporated under reduced pressure to afford ***m*-PO-N3** (5.34 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.18-7.14 (t, 1H), 6.50-6.43 (m, 3H), 3.99-3.95 (t, 4H), 3.37-3.34 (t, 4H), 1.89-1.75 (t, 8H).

***p*-PO-N3:** *p*-PO-N3 was synthesized according to the similar procedure to that for *m*-PO-N3 with *p*-PO-Br (6 g, 16 mmol), sodium azide (3.08 g, 47 mmol) and acetone/water (4:1, 160 mL) (3.36 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.81 (s, 4H), 3.98-3.92 (t, 4H), 3.38-3.34 (t, 4H), 2.17-1.77 (m, 8H).

***t*-PO-N3:** *t*-PO-N3 was synthesized according to the similar procedure to that for *m*-PO-N3 with *t*-PO-Br (7 g, 13.2 mmol), sodium azide (4.28 g, 65.8 mmol) and acetone/water (4:1, 160 mL) (4 g, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.06 (s, 3H), 3.96-3.93 (t, 6H), 3.38-3.34 (t, 6H), 1.84-1.78 (m, 12H).

Synthesis of cross-linker PO-N

To a solution of *m*-PO-N3 (1 g, 3.28 mmol) in dry THF (11 mL), 2.4 M solution of $LiAlH_4$ in dry THF (9.8 mL, 19.6 mmol) was slowly added at 0 °C. The reaction mixture was stirred for 1 h at 0 °C and stirred at room temperature for 12 h. The reaction mixture was quenched following the Fieser work-up. DI water and NaOH aqueous (in DI water) were added dropwise at 0 °C. The mixture was stirred for 15 min at room temperature. Then, anhydrous Na_2SO_4 was added and the mixture was stirred at room temperature for 15 min. The mixture was filtered to afford ***m*-PO-N** (720 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.26-7.13 (t, 1H), 6.50-6.45 (m, 3H), 3.97-3.94 (t, 4H), 2.78-2.75 (t, 4H), 1.84-1.58 (t, 8H), 1.33 (Br, 4H).

***p*-PO-N:** *p*-PO-N was synthesized according to the similar procedure to that for *m*-PO-N with *p*-PO-N3 (1 g, 3.28 mmol), 2.4 M solution of $LiAlH_4$ in dry THF (9.8 mL, 19.6 mmol) and THF (4:1, 160 mL) (645 mg, 78%). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.81 (s, 4H), 3.92 (t, 4H), 2.76-2.74 (t, 4H), 1.81-1.77 (m, 4H), 1.62-1.59 (m, 4H), 1.34 (Br, 4H).

***t*-PO-N**: *t*-PO-N was synthesized according to the similar procedure to that for *m*-PO-N with *t*-PO-N3 (1 g, 2.4 mmol), 2.4 M solution of $LiAlH_4$ in dry THF (9.6 mL, 19.2 mmol) and THF (8 mL) (650 mg, 80%). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.06 (s, 3H), 3.94-3.91 (t, 6H), 2.78-2.74 (t, 6H), 1.81-1.78 (m, 6H), 1.62-1.60 (m, 6H), 1.37 (Br, 6H).

5. OTFT device fabrication

The OTFTs were fabricated with TGBC configurations. The Au electrode was thermally evaporated onto glass, with a thickness of 50 nm using a shadow mask to configure the width (*W*) and length (*L*) of the electrodes as 1000 and 40 µm, respectively. The Y5-TA-Cl monomer solution was prepared by dissolving 6.7 mg of Y5-TA-Cl in CF and stirred 4 h. 0.1 M PO-N (in CF) was added to the Y5-TA-Cl solution by stoichiometric ratio of 1:1. After treatment of UV–ozone for 20 min, the glass/Au patterned substrate was spin-coated with the Y5-TA-Cl monomer solution and annealed 130 °C for 20 min in nitrogen-filled gloves box. The film thicknesses of a series of PY-*x*-TIPO polymers were in the range of 65 nm, identically. Then, the PMMA dielectric layer was deposited onto the polymer film by spin-coating the solution (80 mg/mL in butyl acetate) and annealed 80 °C for 2 h. Finally, the Al electrode was thermally evaporated onto the PMMA dielectric layer for gate electrode. The measurement was conducted with a Keithley 4200 semiconductor parameter analyzer under ambient conditions.

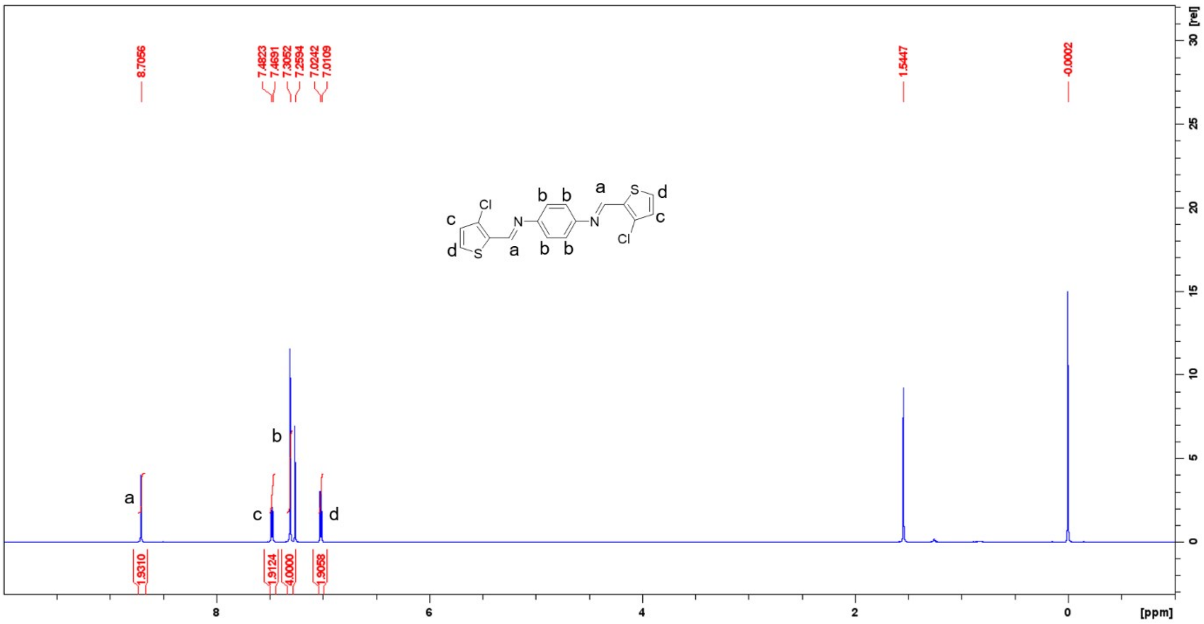


Fig. S1 ^{1}H NMR spectrum of TIP-Cl.

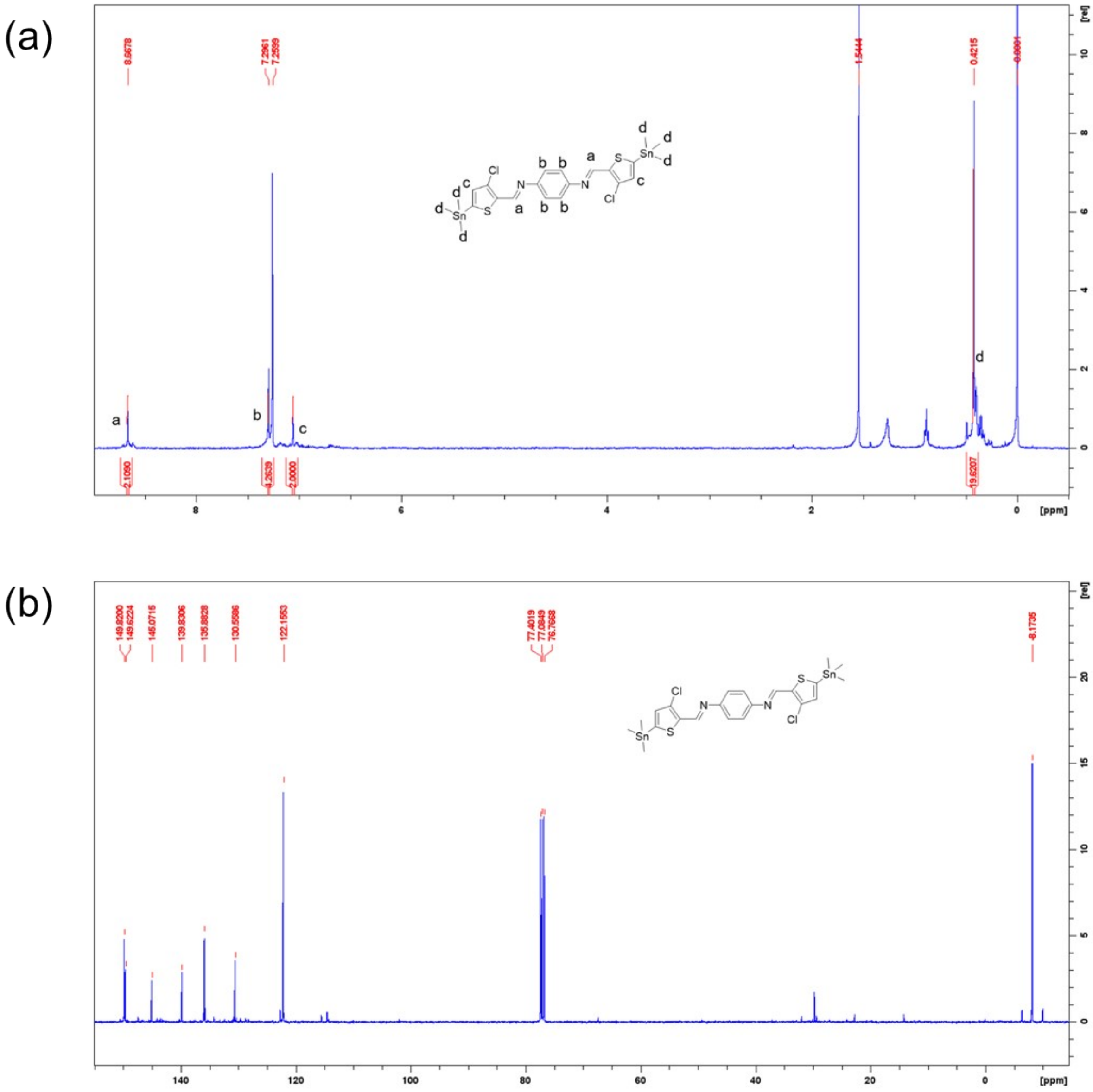


Fig. S2 (a) ^{1}H and (b)^{13}C NMR spectrum of TIP-Cl-ditin.

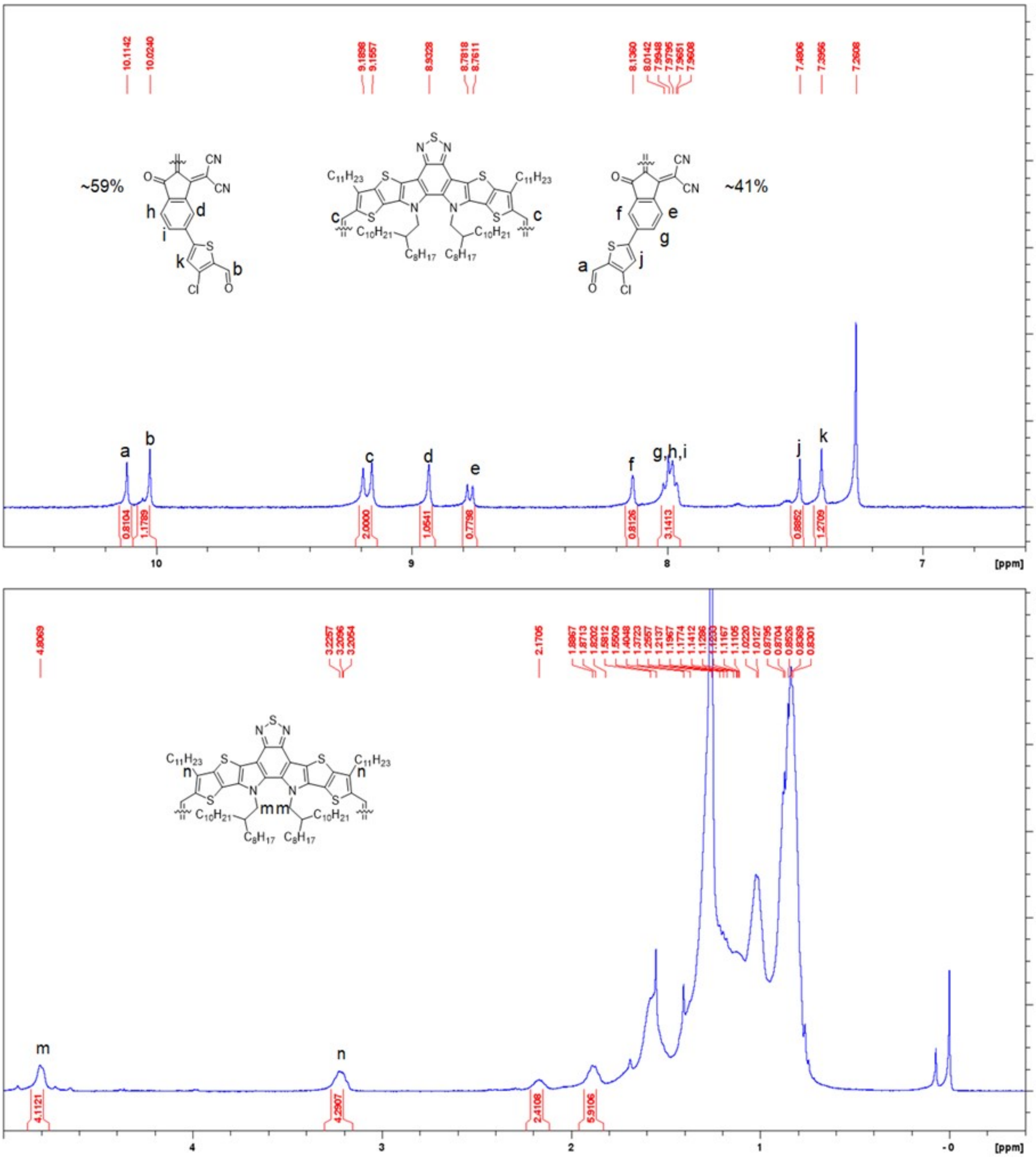


Fig. S3 ^{1}H NMR spectrum of Y5-TA-Cl.

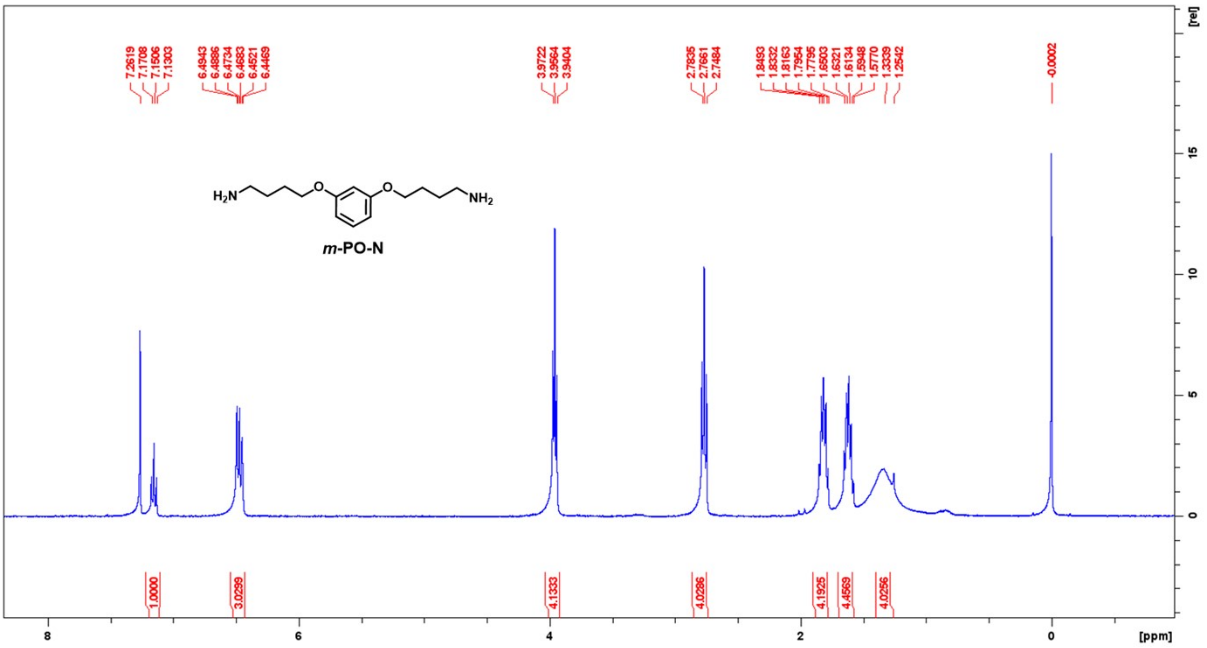


Fig. S4 ^{1}H NMR spectrum of *m*-PO-N.

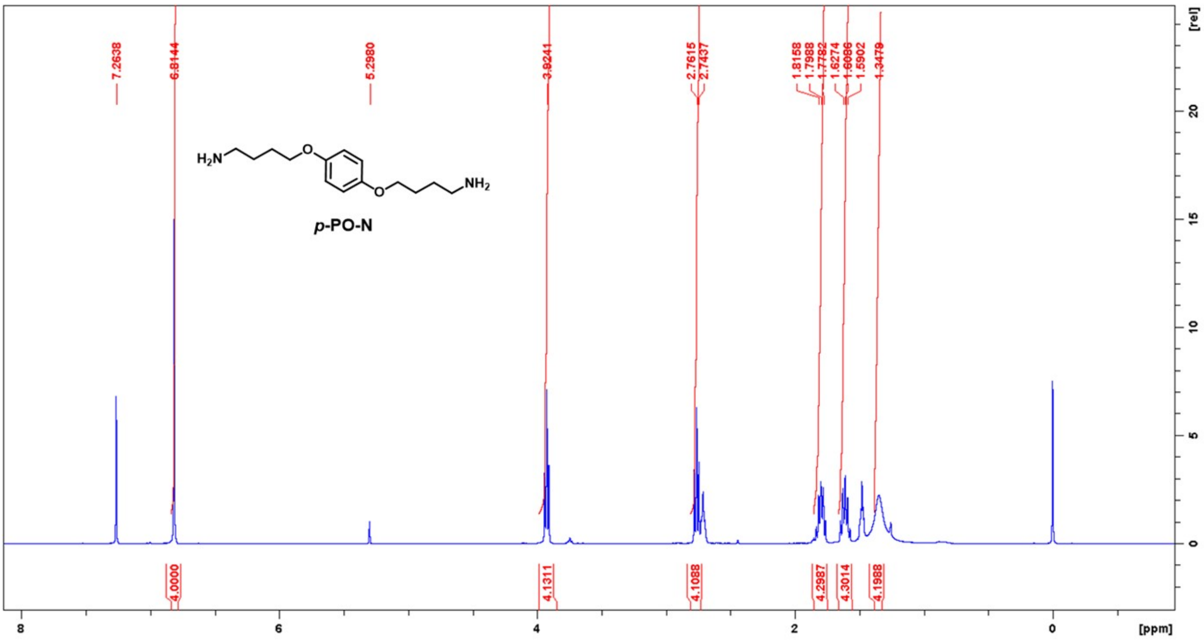


Fig. S5 ^{1}H NMR spectrum of *p*-PO-N.

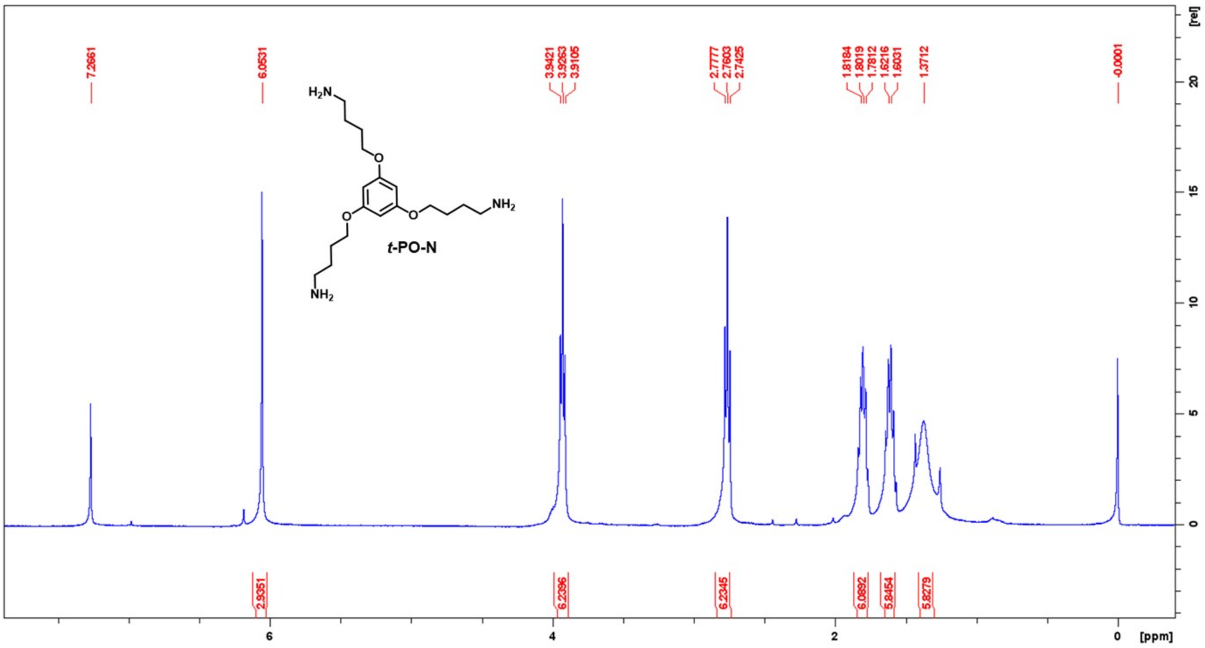


Fig. S6 ^{1}H NMR spectrum of *t*-PO-N.

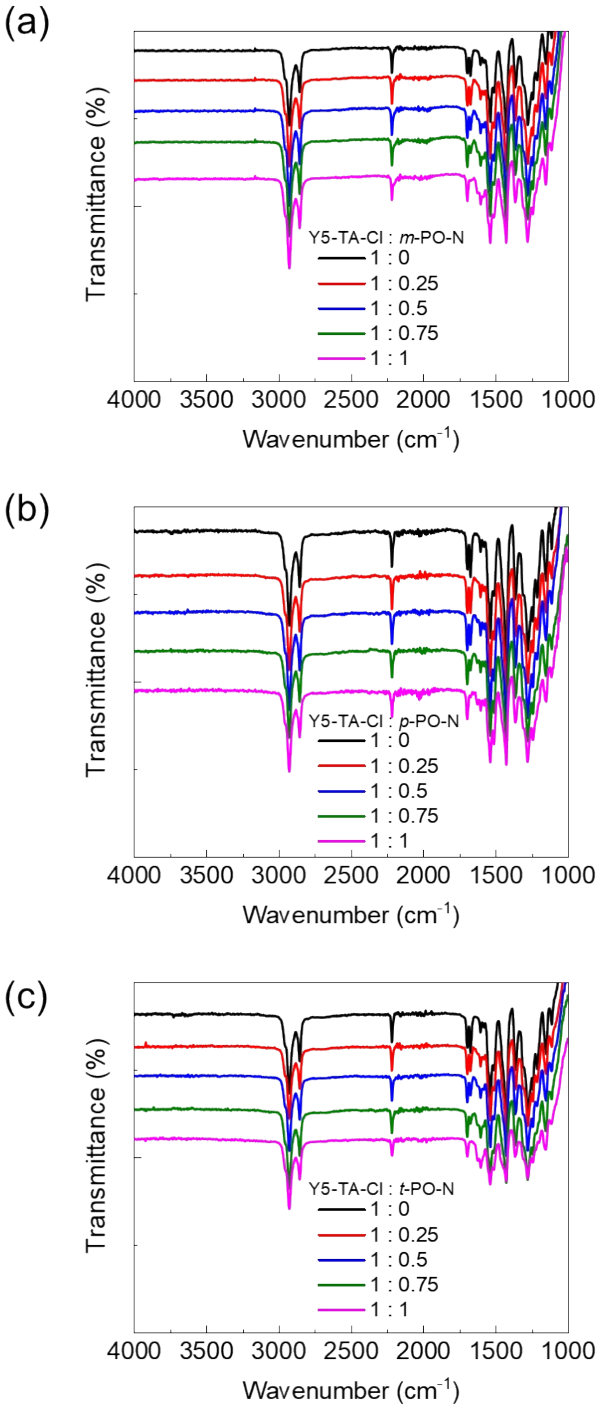
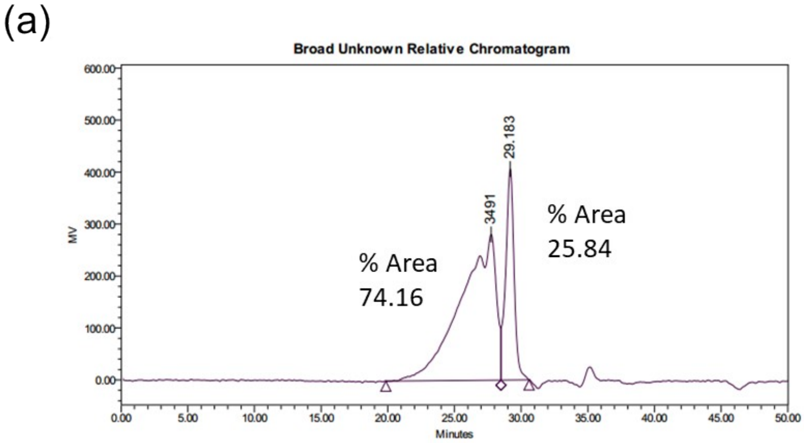
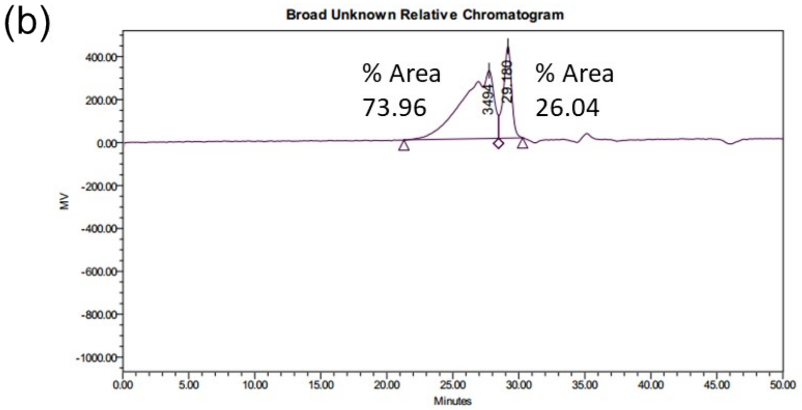


Fig. S7 FT-IR spectra of Y5-TA-Cl with (a) *m*-PO-N, (b) *p*-PO-N, and (c) *t*-PO-N annealed film in various stoichiometric ratios (Y5-TA-Cl:PO-N = 1:0, 1:0.25, 1:0.5, 1:0.75, 1:1).



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		5971	10004	3491	19057	33411	1.675378	1.904889	3.339657



Broad Unknown Relative Peak Table

	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		5640	8461	3494	13631	20912	1.500041	1.611019	2.471564

Fig. S8 GPC curves of (a) PY-*m*-TIPO and (b) PY-*p*-TIPO.

Table S1 Optical properties of Y5-TA-Cl and series of degradable polymers.

Material	λ_{max} [nm]	λ_{onset} [nm]	Bg^{opt} [eV]
Y5-TA-Cl	817	912	1.36
PY-*m*-TIPO	788	865	1.43
PY-*p*-TIPO	790	867	1.43
PY-*t*-TIPO	792	870	1.43

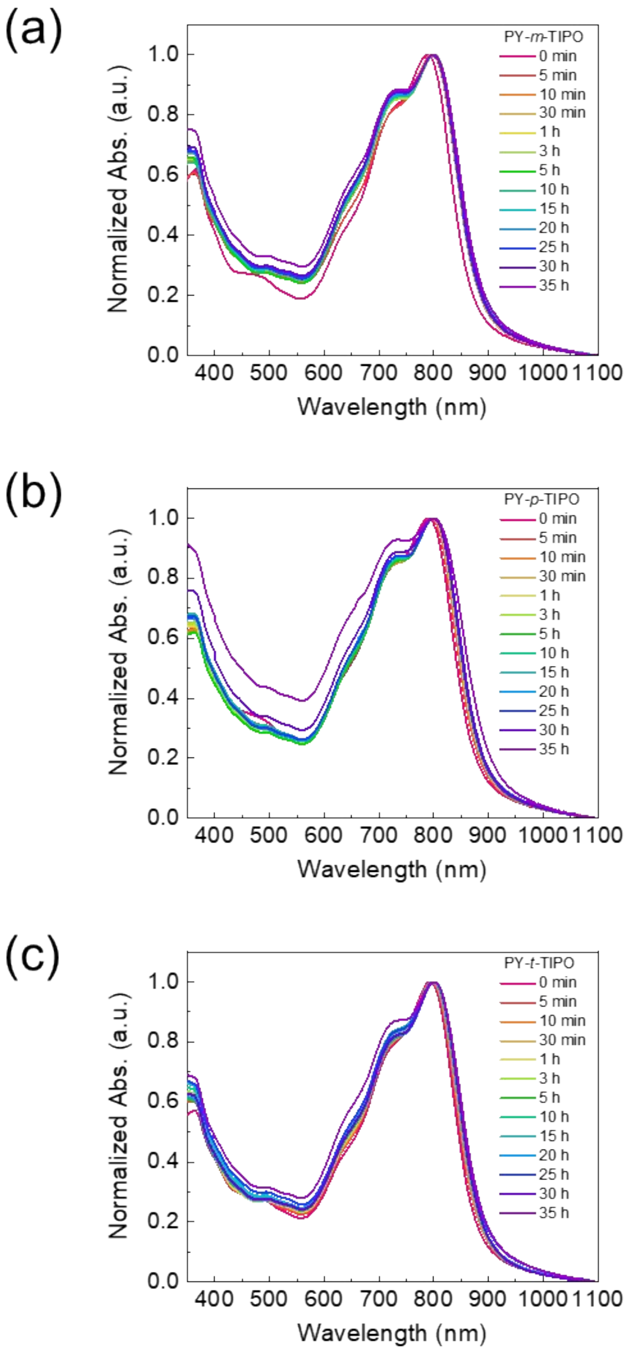


Fig. S9 The normalized UV–Vis absorption of films based on (a) PY-*m*-TIPO, (b) PY-*p*-TIPO and (c) PY-*t*-TIPO in 0.1 M TFA during degradation procedure.

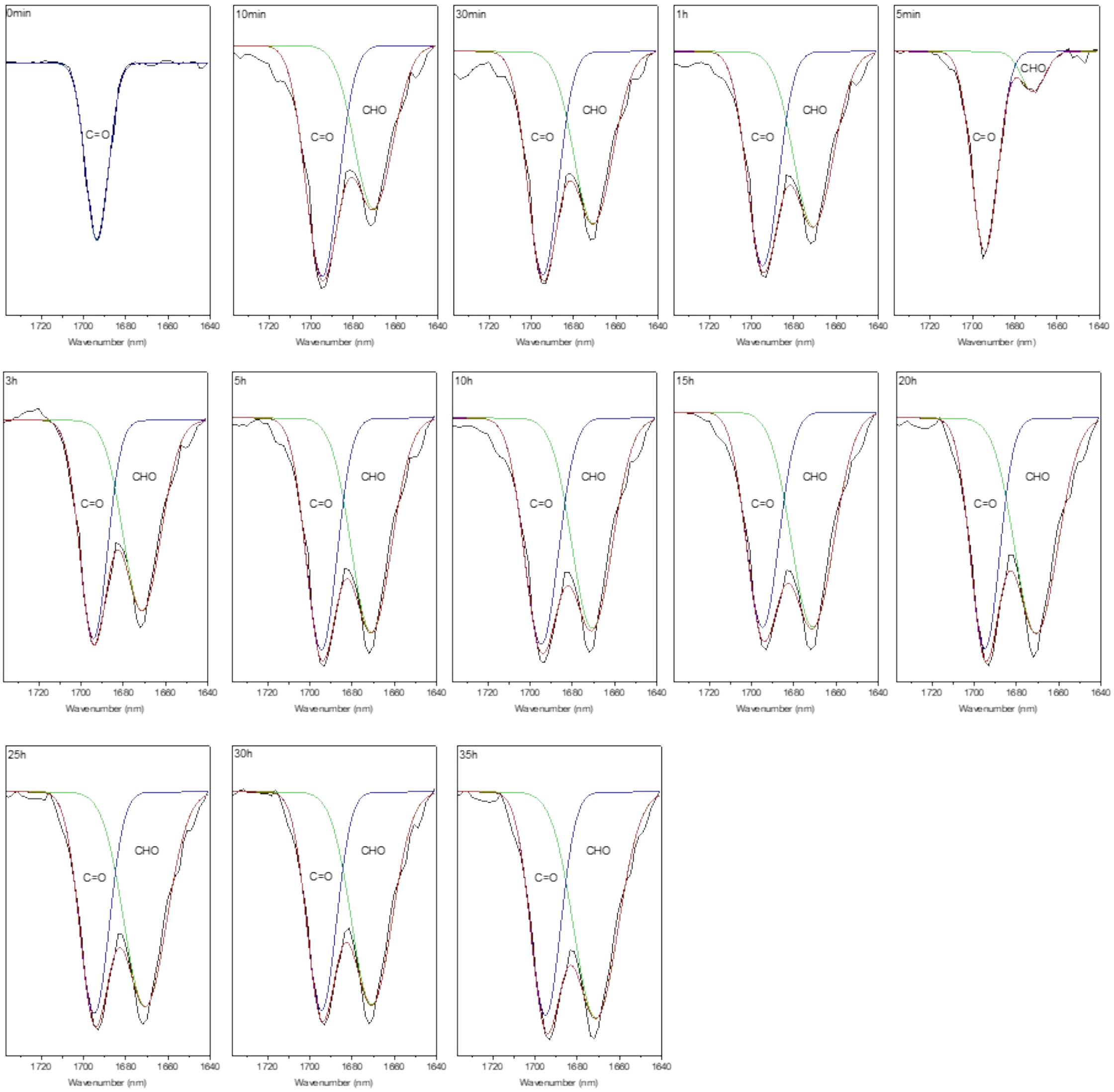


Fig. S10 The deconvoluted FT-IR spectra of film based on PY-*m*-TIPO in 0.1 M TFA during degradation procedure.

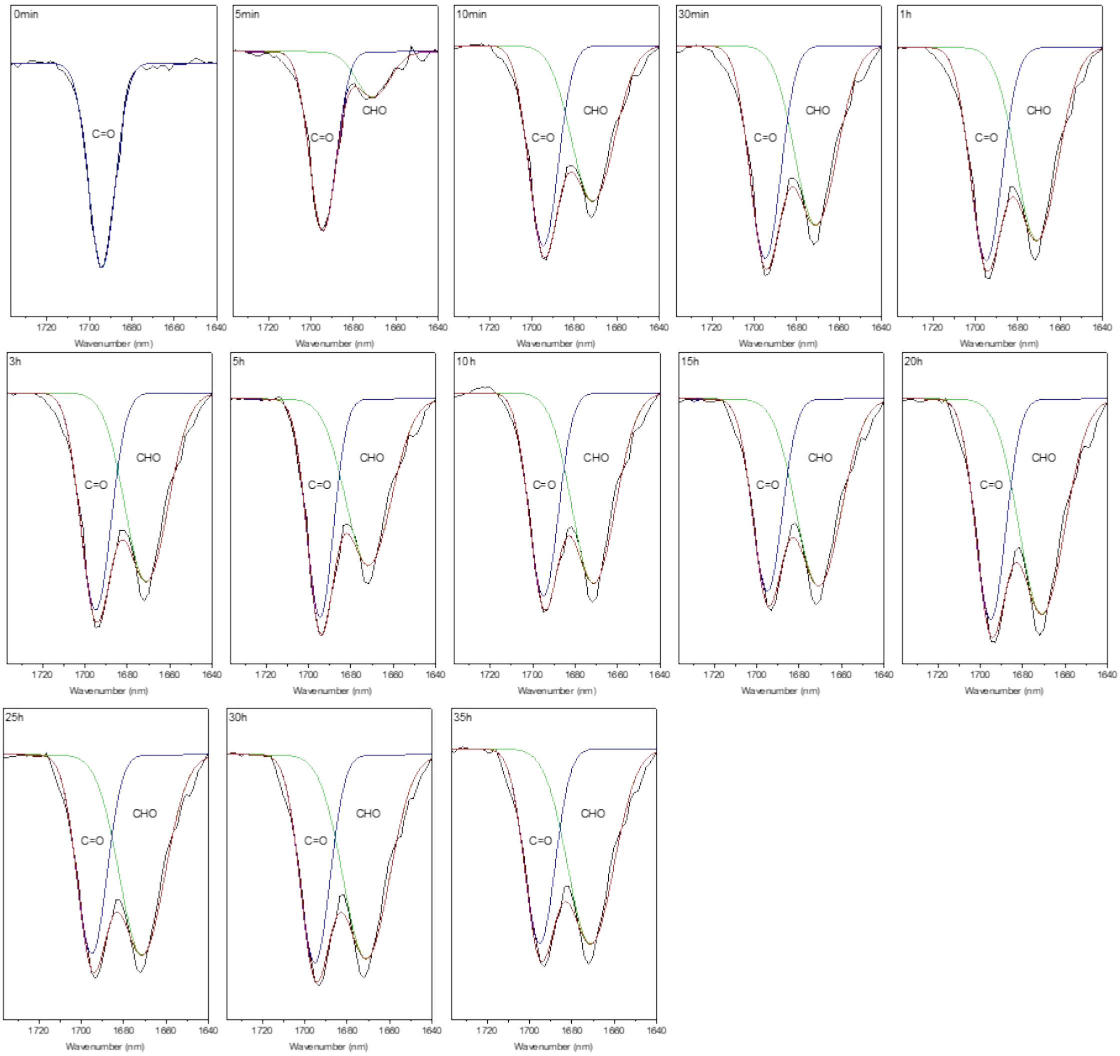


Fig. S11 The deconvoluted FT-IR spectra of film based on PY-*p*-TIPO in 0.1 M TFA during degradation procedure.

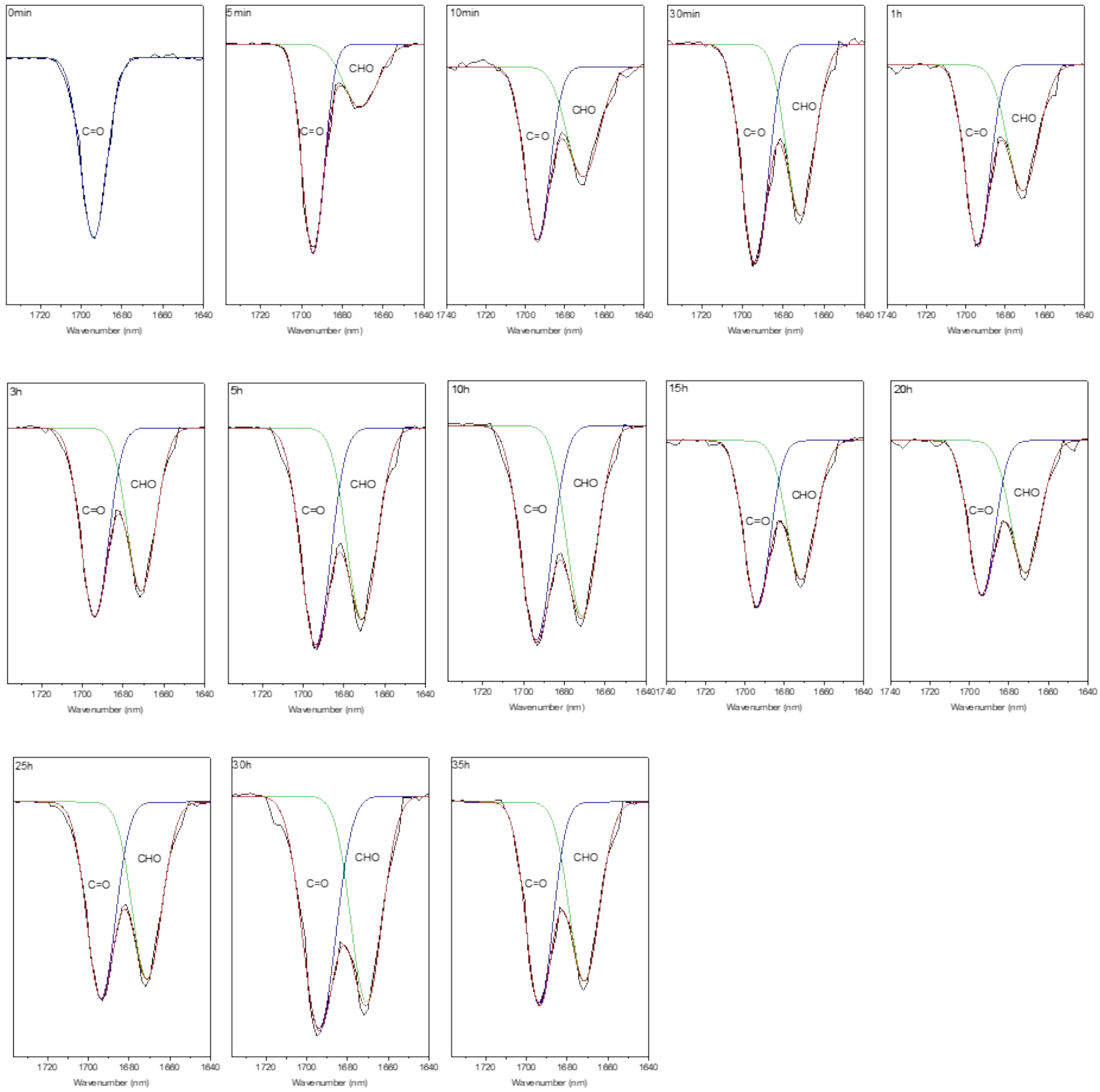


Fig. S12 The deconvoluted FT-IR spectra of film based on PY-*t*-TIPO in 0.1 M TFA during degradation procedure.

Table S2 Comparison of integrated peaks in FT-IR spectra and the polymerization yield defined by the ratio of integrated areas of aldehyde peaks in 0.1 M TFA during degradation procedure. of PY-*m*-TIPO.

Material	Degradation time	Normalized value of integrated area $[\frac{CHO, 1679\ cm^{-1}}{C=O, 1695\ cm^{-1}}]$
PY-*m*-TIPO	0 min	0
	5 min	0.18
	10 min	0.83
	30 min	0.98
	1 h	1.04
	3 h	1.19
	5 h	1.21
	10 h	1.26
	15 h	1.30
	20 h	1.38
	25 h	1.39
	30 h	1.33
	35 h	1.48

Table S3 Comparison of integrated peaks in FT-IR spectra and the polymerization yield defined by the ratio of integrated areas of aldehyde peaks in 0.1 M TFA during degradation procedure. of PY-*p*-TIPO.

Material	Degradation time	Normalized value of integrated area $[\frac{CHO, 1679\ cm^{-1}}{C=O, 1695\ cm^{-1}}]$
PY-*p*-TIPO	0 min	0
	5 min	0.32
	10 min	1.13
	30 min	1.15
	1 h	1.20
	3 h	1.22
	5 h	1.31
	10 h	1.40
	15 h	1.48
	20 h	1.48
	25 h	1.51
	30 h	1.52
	35 h	1.52

Table S4 Comparison of integrated peaks in FT-IR spectra and the polymerization yield defined by the ratio of integrated areas of aldehyde peaks in 0.1 M TFA during degradation procedure. of PY-*t*-TIPO.

Material	Degradation time	Normalized value of integrated area $[\frac{CHO, 1679\ cm^{-1}}{C=O, 1695\ cm^{-1}}]$
PY-*t*-TIPO	0 min	0
	5 min	0.35
	10 min	0.47
	30 min	0.84
	1 h	0.87
	3 h	0.89
	5 h	0.91
	10 h	0.89
	15 h	0.92
	20 h	0.98
	25 h	0.94
	30 h	1.01
	35 h	1.00

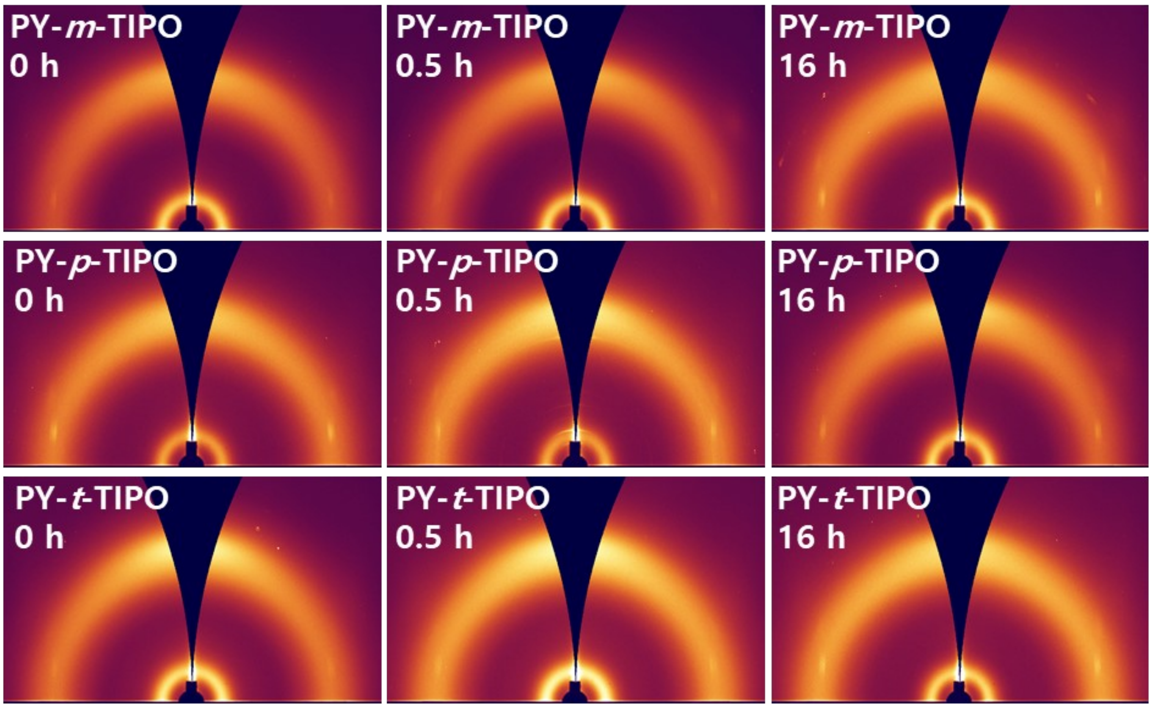


Fig. S13 2D-GIWAXS patterns of degradable polymers during degradation procedure.

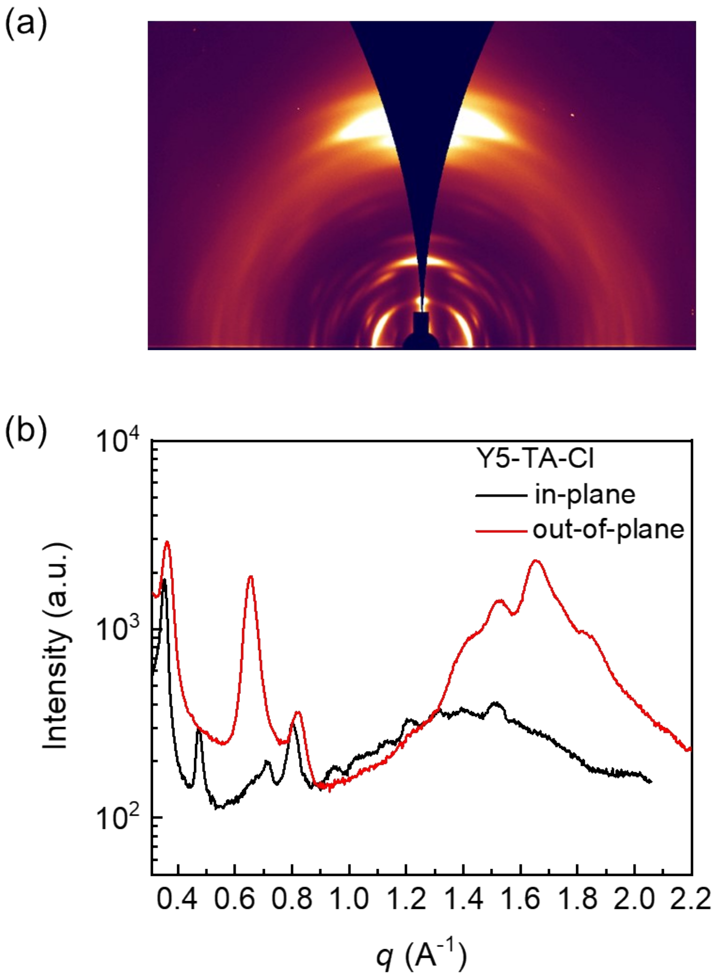


Fig. S14 2D-GIWAXS patterns of pristine films based on (a) Y5-TA-Cl. (b) Their corresponding in-plane and out-of-plane line-cut profiles.

Table S5 Crystallographic parameter from 2D-GIWAXS measurements for Y5-TA-Cl and series of degradable polymer films.

Sample	Degradation	In-plane		Out-of-plane	
	time[a]	*d*(100)	L_C(100)	*d*(π-π)	L_C(π-π)
Y5-TA-Cl	0 h	17.99	211.77	3.79	49.38
PY-*m*-TIPO	0 h	19.44	38.699	3.97	12.21
	0.5 h	19.69	45.66	3.96	12.26
	16 h	20.01	45.81	3.99	11.23
PY-*p*-TIPO	0 h	19.39	44.47	4.02	11.83
	0.5 h	19.70	43.48	3.98	11.88
	16 h	20.29	45.53	3.95	12.17
PY-*t*-TIPO	0 h	19.22	42.73	3.96	12.52
	0.5 h	19.45	41.94	3.99	12.17
	16 h	20.14	45.887	4.00	11.69

[a] Exposure to vapor from a 0.1 M TFA solution.

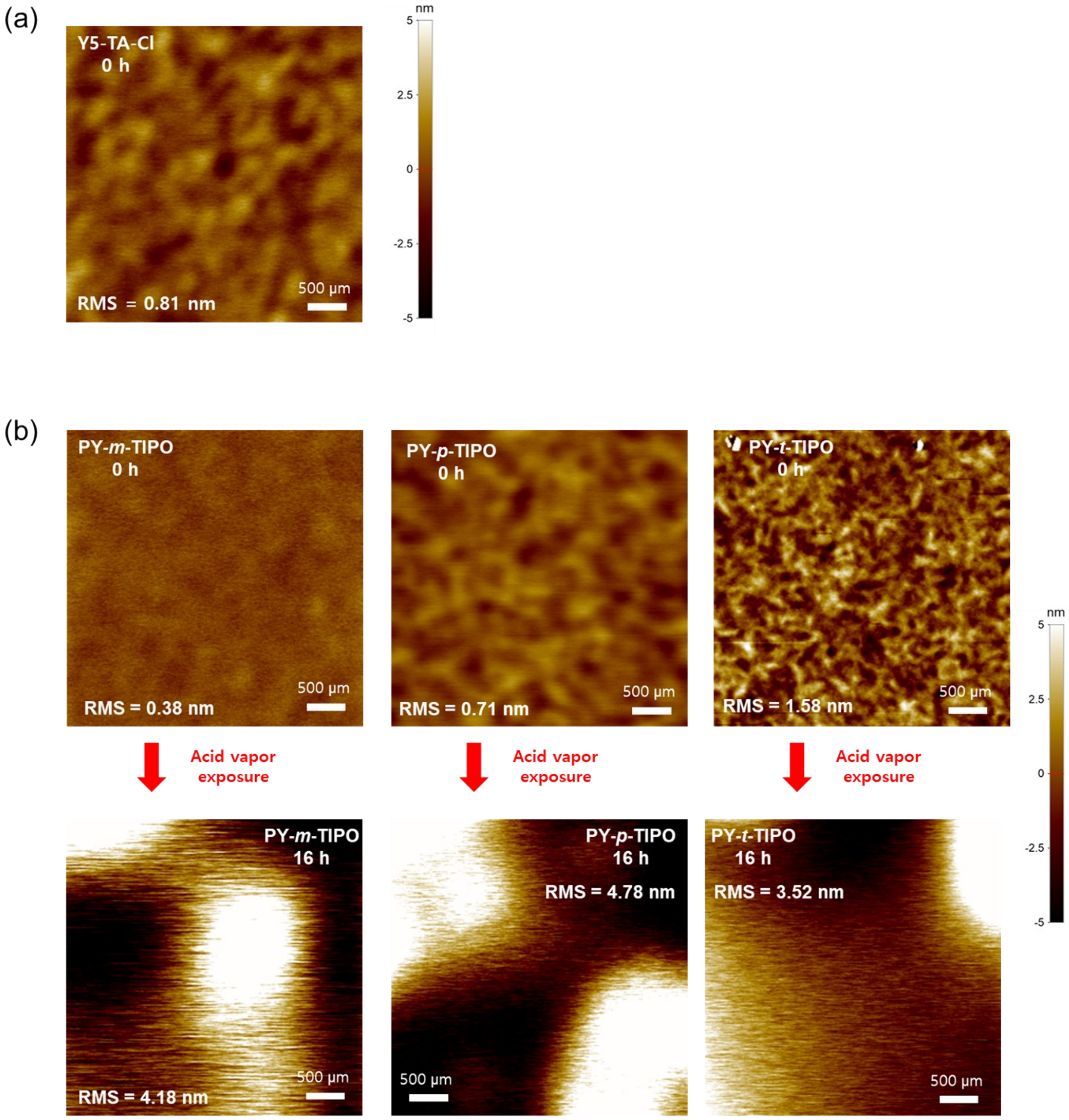


Fig. S15 AFM topography images of (a) Y5-TA-Cl, (b) PY-*m*-TIPO, PY-*p*-TIPO, and PY-*t*-TIPO after and before acid vapor exposure.

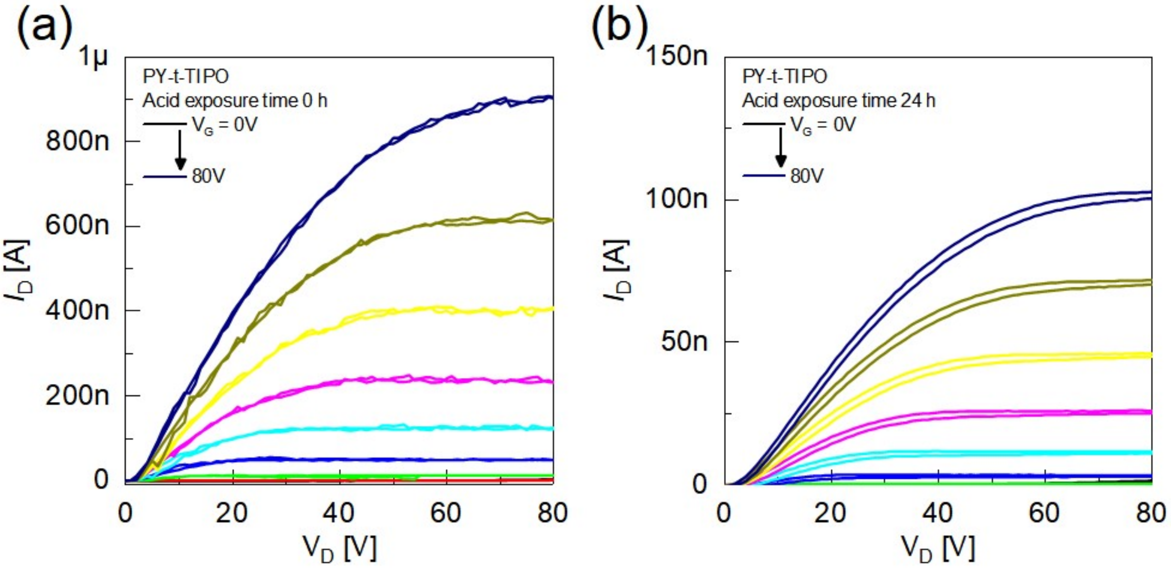


Fig. S16 Output characteristics of PY-*t*-TIPO with before and after acid treatment.

References

1. W. Wang, Q. Wu, R. Sun, J. Guo, Y. Wu, M. Shi, W. Yang, H. Li and J. Min, *Joule*, 2020, **4**, 1070-1086.
2. Y. Garcia, Y. Boland, P. Hertsens and J. Marchand-Brynaert, *Synthesis*, 2006, **2006**, 1504-1512.
3. H. Jin, K. Kim, S. Park, J. Rhee, H. Ahn, D. J. Kim, K. Kim, J. H. Noh, T. S. Kim, E. Y. Shin and H. J. Son, *Adv. Funct. Mater.*, 2023, **33**.
4. S. Selvarani, P. Rajakumar, S. Nagaraj, M. Choudhury and D. Velmurugan, *New J. Chem.*, 2018, **42**, 12684-12691.