

Supporting Information

Monomeric and aggregation emissions of tetraphenylethene in a photo-switchable polymer controlled by cyclization of diarylethene and solvent conditions

Ravinder Singh,^a Hsin-Yen Wu,^a Atul Kumar Dwivedi,^a Ashutosh Singh,^a Chien-Min Lin,^a Putikam
Raghunath,^b Ming-Chang Lin,^b Tung-Kung Wu,^c Kung-Hwa Wei^a and Hong-Cheu Lin^{*a}

^a Department of Materials Science & Engineering, National Chiao Tung University, Hsinchu, Taiwan.

^b Center for Interdisciplinary Molecular Science, Department of Applied Chemistry, National Chiao
Tung University, Hsinchu 300, Taiwan.

^c Department of Biological Science & Technology, National Chiao Tung University, Hsinchu, Taiwan.

*E-mail: linhc@mail.nctu.edu.tw

List of contents:

1. Figs. S1 & S2	-----	page S3
2. Figs. S3 & S4	-----	page S4
3. Figs. S5 & S6	-----	page S5
4. Figs. S7 & S8	-----	page S6
5. Figs. S9 & S10 (Table)	-----	page S7-S8
6. Figs. S11-S13	-----	page S9-S10
7. NMR (^1H & ^{13}C) (Figs. S14 to S21)	-----	page S11-S17
8. HRMS (ESI data) (Fig. S22)	-----	page S18
9. HRMS (ESI data) (Fig. S23)	-----	page S19
10. HRMS (ESI data) (Fig. S24)	-----	page S20
11. HRMS (ESI data) (Fig. S25)	-----	page S21
12. HPLC data (Figs. S26 & S27)	-----	page S22
13. GPC data (Fig. S28)	-----	page S23

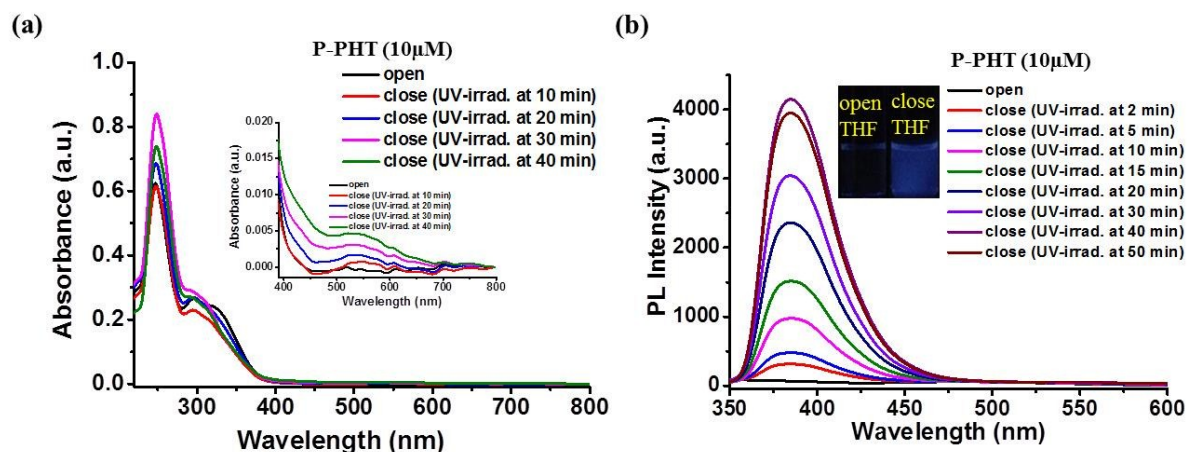


Fig. S1 P-PHT in THF before and after UV-irradiation, (a) UV-Vis spectral changes of P-PHT (open to close). (b) PL spectral changes of P-PHT (open to close). Inset: Photoimages of P-PHT 0 min and 40 min. ($\lambda_{\text{ex}} = 320$ nm for PL exp.)

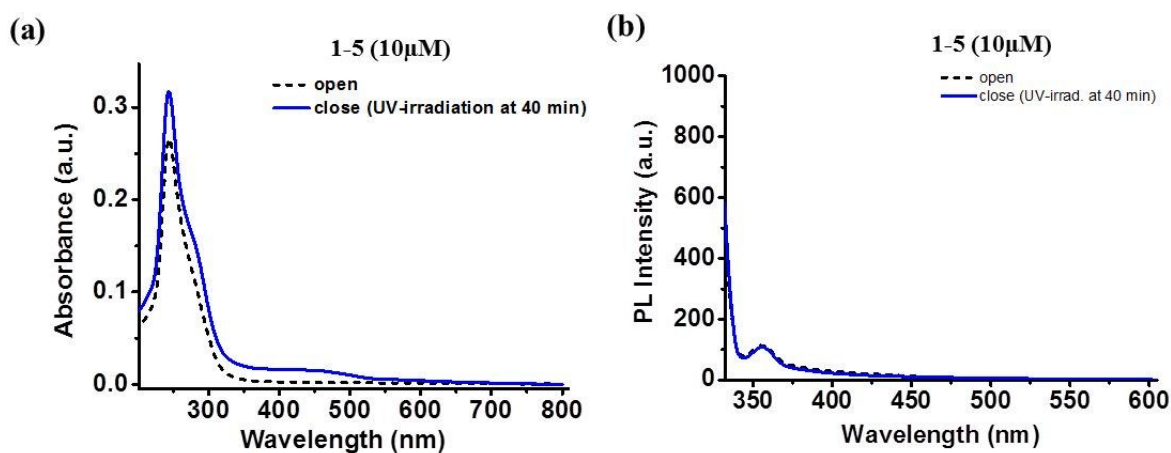


Fig. S2 Compound 1-5 in THF before and after UV-irradiation, (a) UV-Vis spectral changes of compound 1-5 (open to close). (b) PL spectral changes of compound 1-5 (open to close). ($\lambda_{\text{ex}} = 320$ nm for PL exp.)

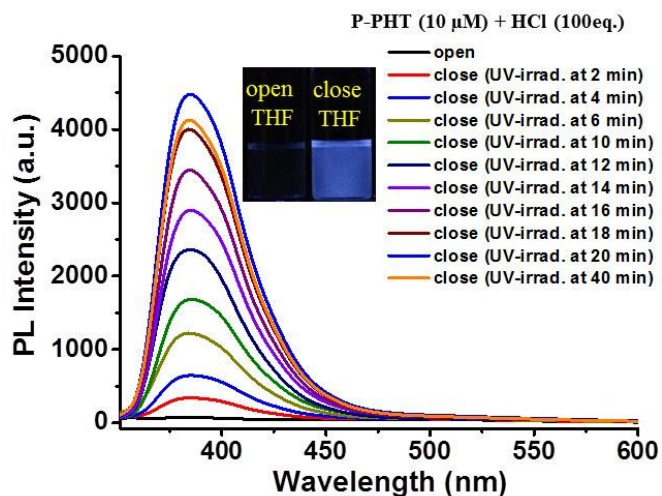


Fig. S3 PL spectral changes of **P-PHT** (open to close form) with **HCL** (100 eq.) before and after UV-irradiation. Inset: Photoimages of **P-PHT** at 0 and 20 min with **HCl** (100eq.). ($\lambda_{\text{ex}} = 320$ nm for PL exp.)

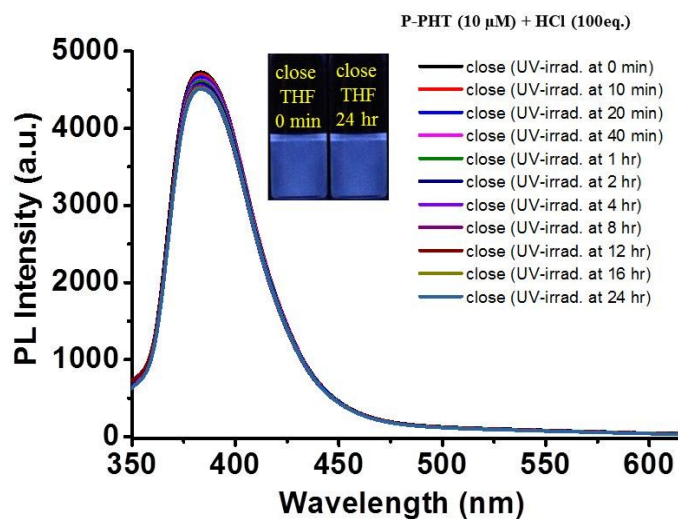


Fig. S4 PL spectral changes of **P-PHT** (close) under acidic condition (**HCl** 100 eq. in **THF**) at different time intervals (from 0 to 24 hr). Inset: Photoimages of **P-PHT**(close) at 0 min and 24 hr. ($\lambda_{\text{ex}} = 320$ nm for PL exp.)

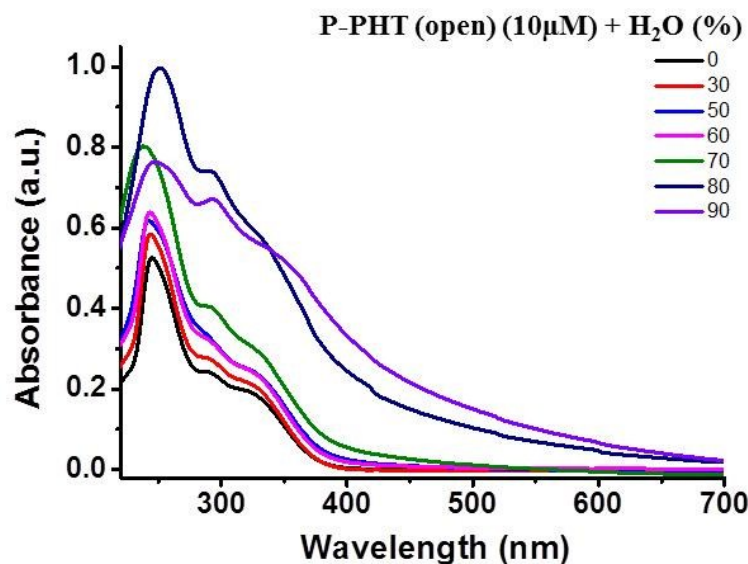


Fig. S5 UV-Vis spectral changes of **P-PHT** (open) in THF by increasing water contents.

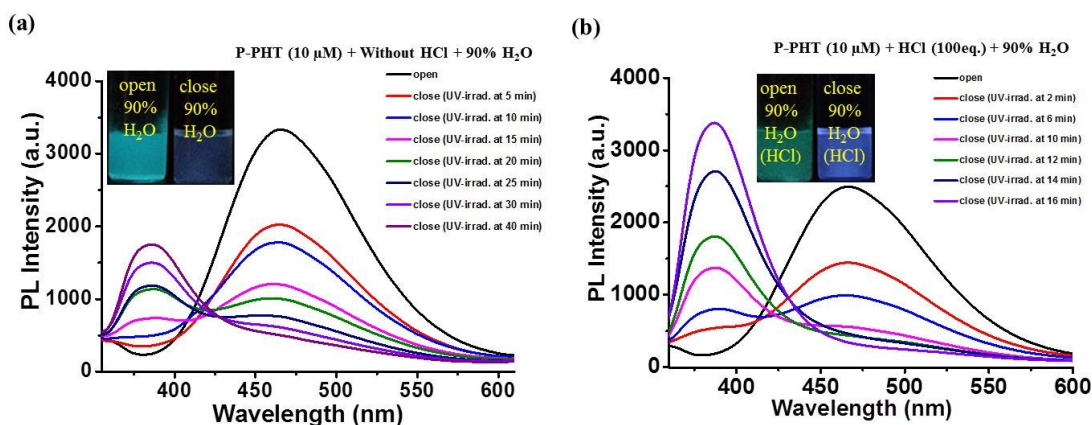


Fig. S6 **P-PHT** at 90% water content before and after UV-irradiation (at $\lambda = 346$ nm), (a) and (b) PL spectral changes of **P-PHT** (90% H₂O) from open to close form upon UV-irradiation without and with HCl (100eq.), respectively. Insets: Photoimages of **P-PHT** (90% H₂O) at 0, 40 min (UV-irradiation) without HCl, and at 0, 20 min (UV-irradiation) with HCl, respectively. ($\lambda_{\text{ex}} = 320$ nm for PL exp.)

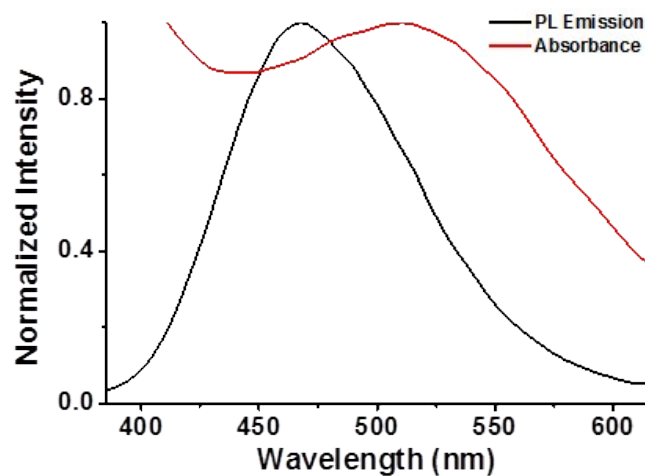


Fig. S7 Spectral overlaps between AIE emission of TPE and absorption of cyclized DAE unit in **P-PHT**.

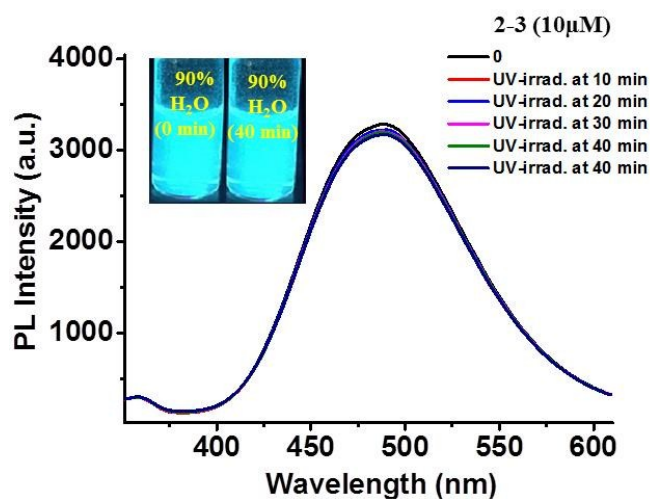


Fig. S8 PL spectral changes of compound **2-3** at 90% water content after UV-irradiation (40 min and $\lambda = 346$ nm). Insets: Photoimages of compound **2-3** (90% H_2O) at 0 min and 40 min (UV-irradiation). ($\lambda_{\text{exc}} = 320$ nm for PL exp.)

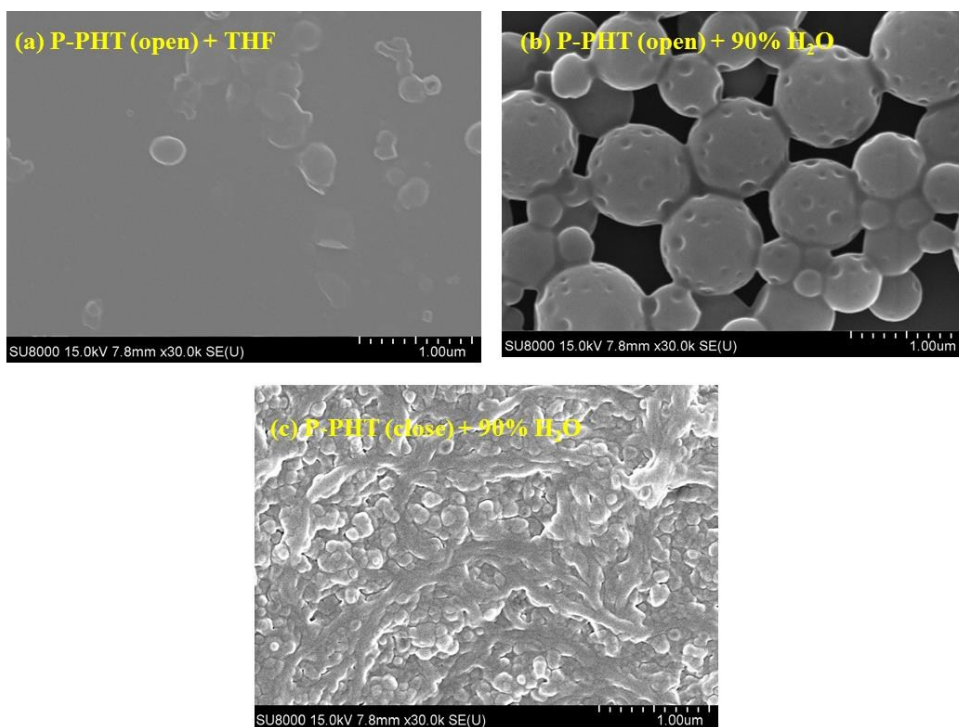


Fig. S9 Morphological images of (a) **P-PHT** (open) in THF (b) **P-PHT** (open) at 90% water content. Upon the UV-Irradiation, (c) **P-PHT** (close) at 90% water content.

P- PHT	Absorption data				
	Excited State	$\lambda_{\text{abs,cal}}$ (nm)	f^{a}	Configuration^b	Weight^c (%)
open form	S1	350.7	0.47	H \rightarrow L	99.3
	S4	286.5	0.12	H-1 \rightarrow L+1	96.7
close form	S1	478.7	0.20	H \rightarrow L	99.5
	S4	350.2	0.48	H-1 \rightarrow L+1	96.7
	S12	284.2	0.12	H-1 \rightarrow L+4	86.2

Fig. (Table) S10 Absorption and Fluorescence maxima, Oscillator strengths, Contributing transitions of open and close forms of **P-PHT** are calculated by B3LYP/6-31G(d) method. (^a Oscillator strength), (^b H and L represent the calculated HOMO and LUMO, respectively; The second highest occupied and lowest unoccupied molecular orbitals denoted as H-1 and L+1, respectively), (^c Only configurations with 5% or greater contribution are included.).

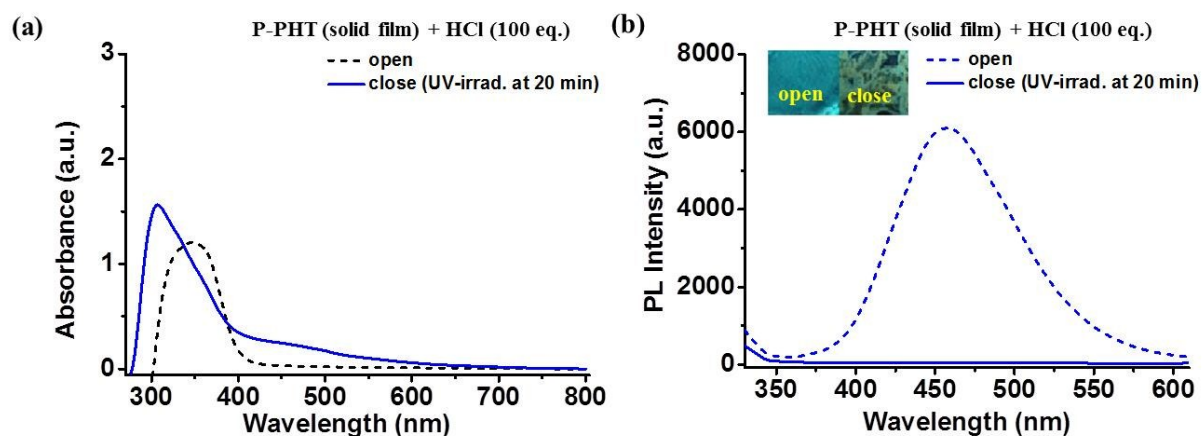


Fig. S11 P-PHT in solid films before and after UV-irradiation under HCL (100 eq.), (a) UV-Vis spectral changes of **P-PHT** (open to close). (b) PL spectral changes of **P-PHT** (open to close). Inset: Photoimages of **P-PHT** at 0 min and 20 min. ($\lambda_{\text{exc}} = 320$ nm for PL exp.)

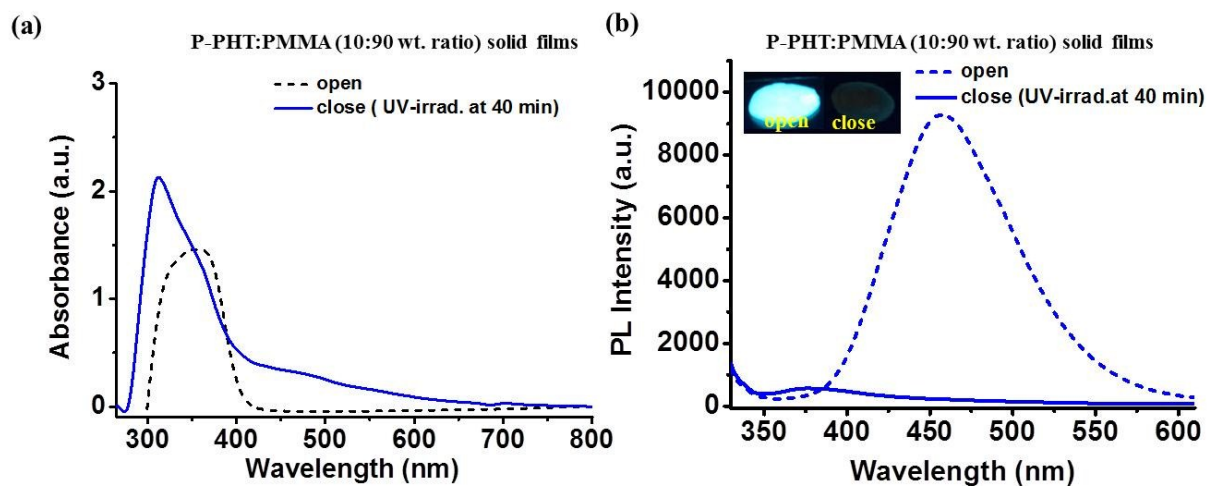


Fig. S12 **P-PHT:PMMA** (10:90 wt. ratio) in solid films before and after UV-irradiation, (a) UV-Vis spectral changes of **P-PHT:PMMA** (10:90 wt. ratio) (open to close). (b) PL spectral changes of **P-PHT:PMMA** (10:90 wt. ratio) (open to close). Inset: Photoimages of **P-PHT:PMMA** (10:90 wt. ratio) at 0 min and 40 min. ($\lambda_{\text{ex}} = 320$ nm for PL exp.)

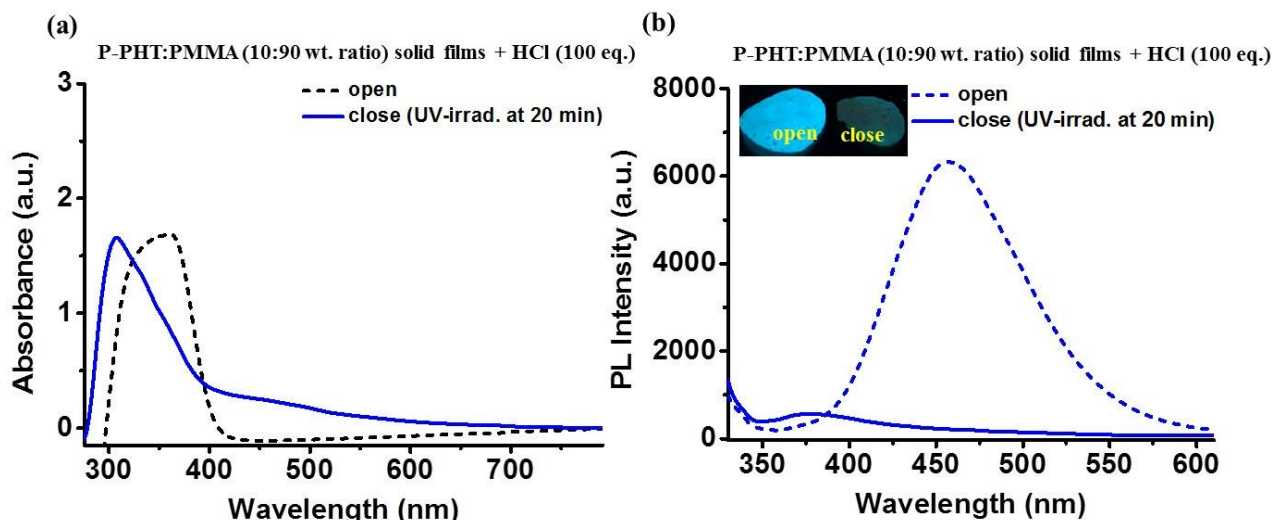


Fig. S13 **P-PHT:PMMA** (10:90 wt. ratio) in solid films before and after UV-irradiation with HCl (100 eq.), (a) UV-Vis spectral changes of **P-PHT:PMMA** (10:90 wt. ratio) (open to close). (b) PL spectral changes of **P-PHT:PMMA** (10:90 wt. ratio) (open to close). Inset: Photoimages of **P-PHT:PMMA** (10:90 wt. ratio) at 0 min and 20 min. ($\lambda_{\text{ex}} = 320$ nm for PL exp.)

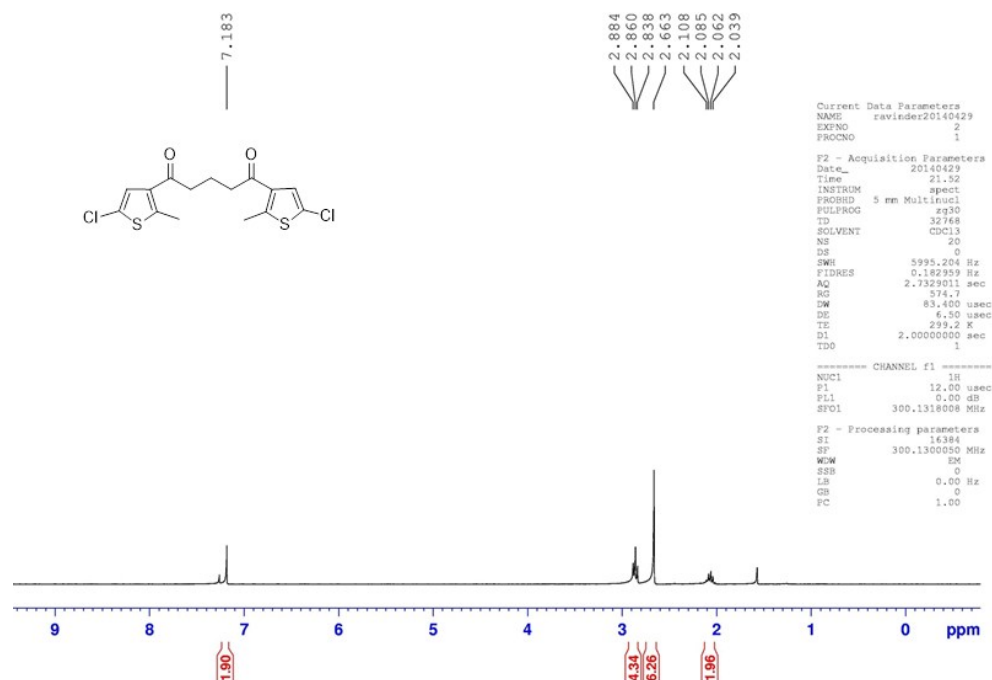


Fig. S14 ¹H-NMR of intermediate 1-1.

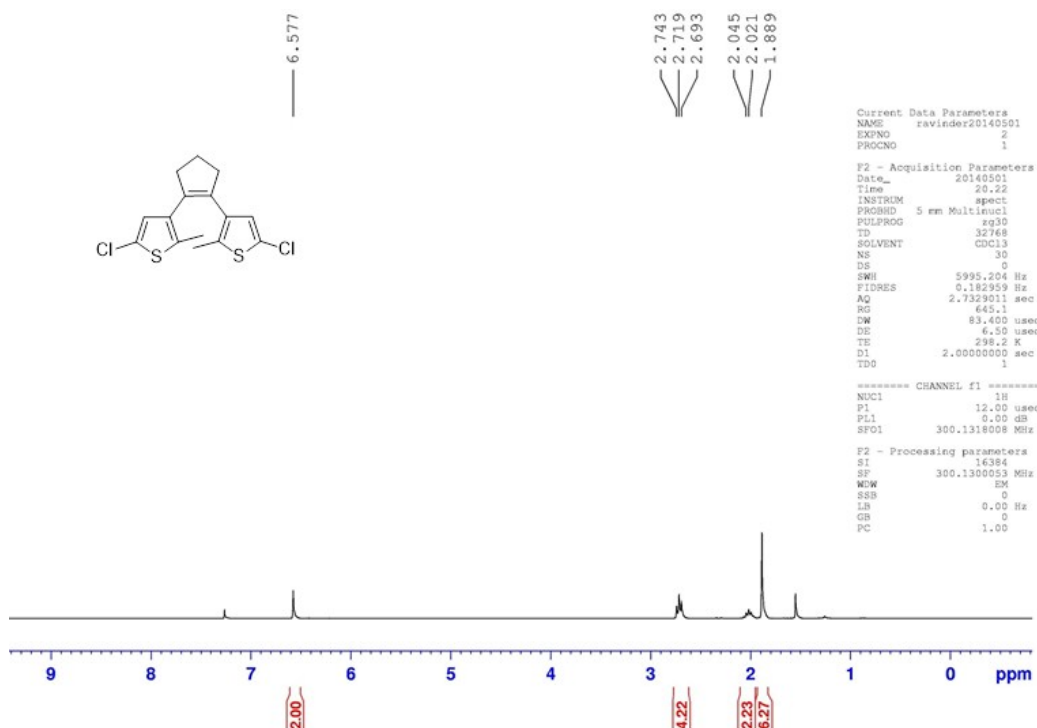


Fig. S15 ¹H-NMR of intermediate 1-2.

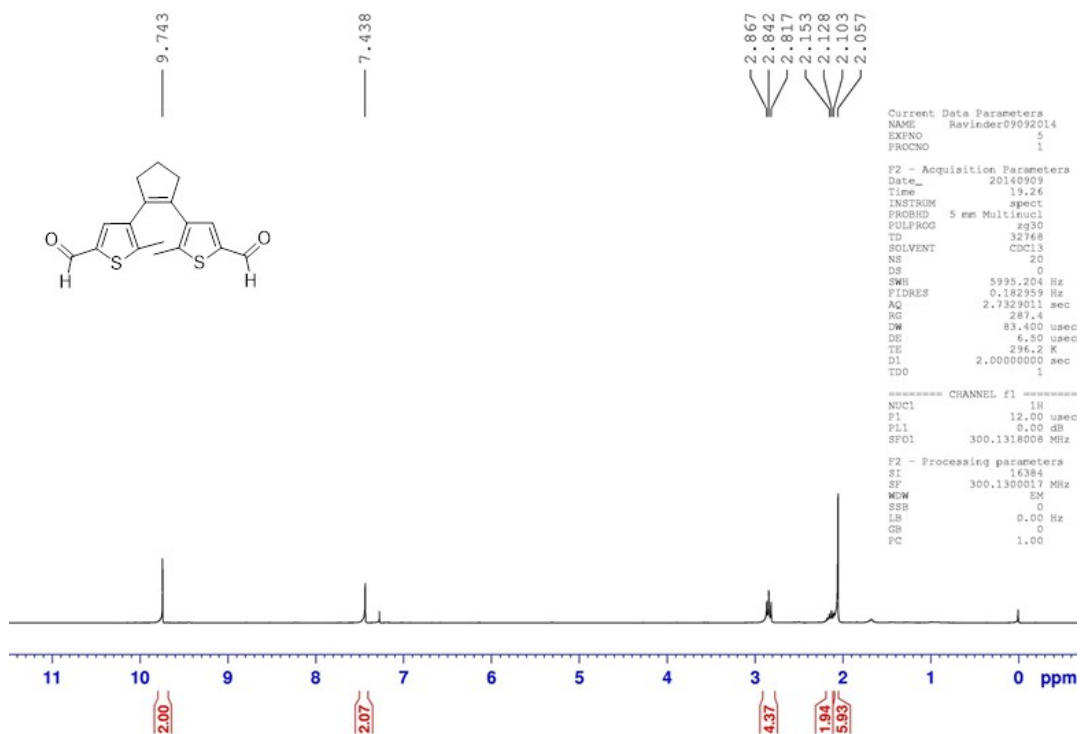


Fig. S16.1 ¹H-NMR of intermediate 1-3.

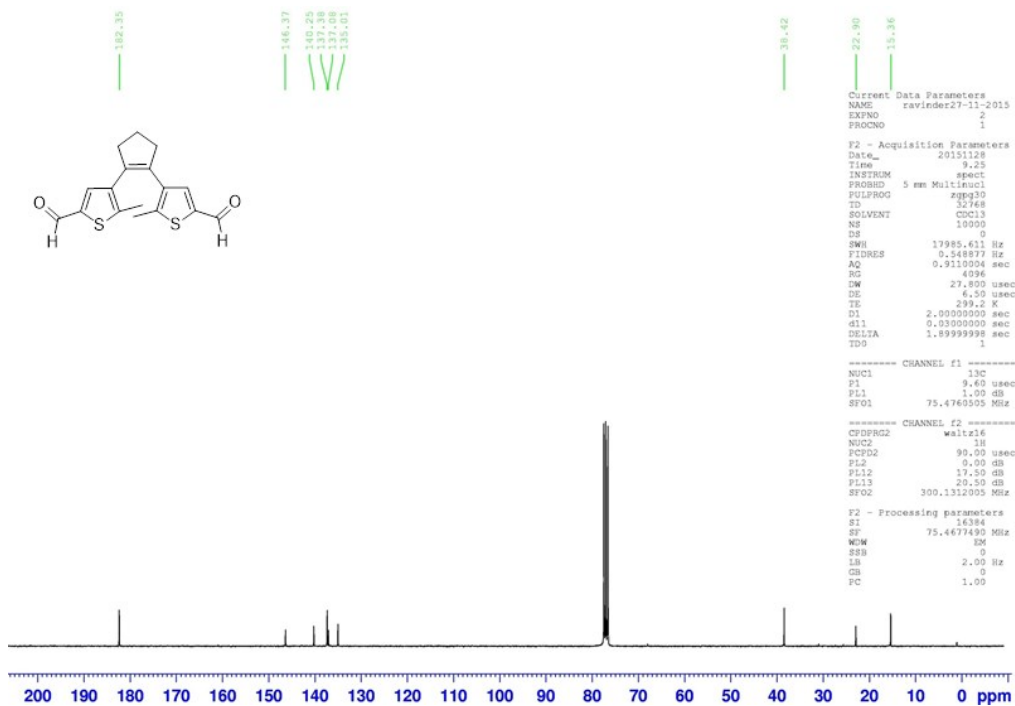


Fig. S16.2 ¹³C-NMR of Intermediate 1-3.

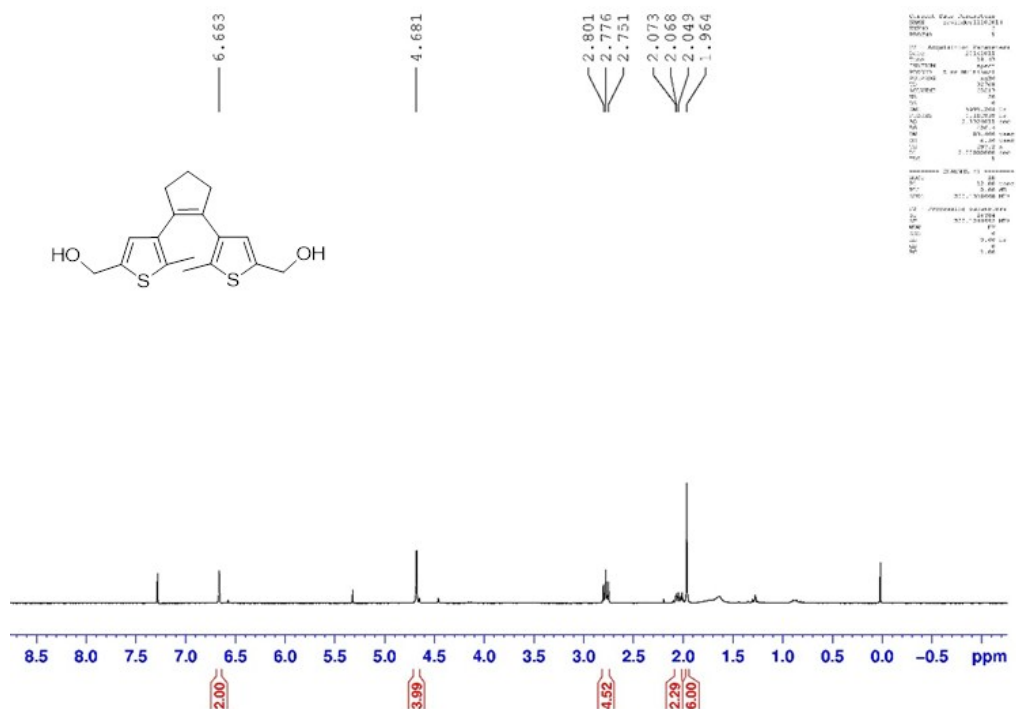


Fig. S17.1 ¹H-NMR of intermediate 1-4.

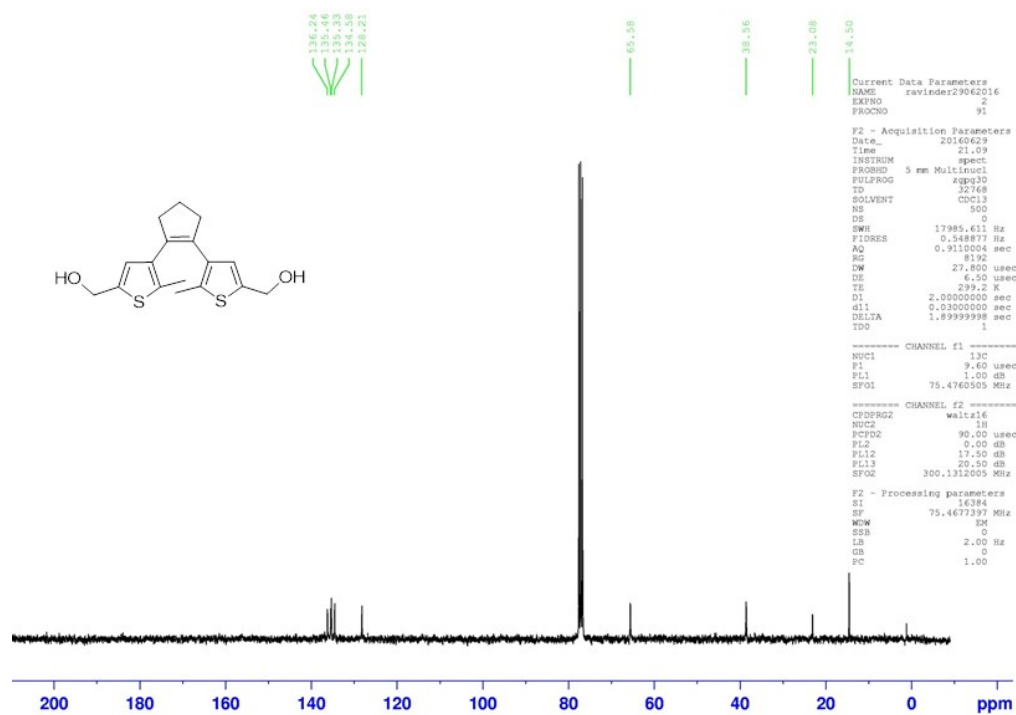


Fig. S17.2 ¹³C-NMR of intermediate 1-4.

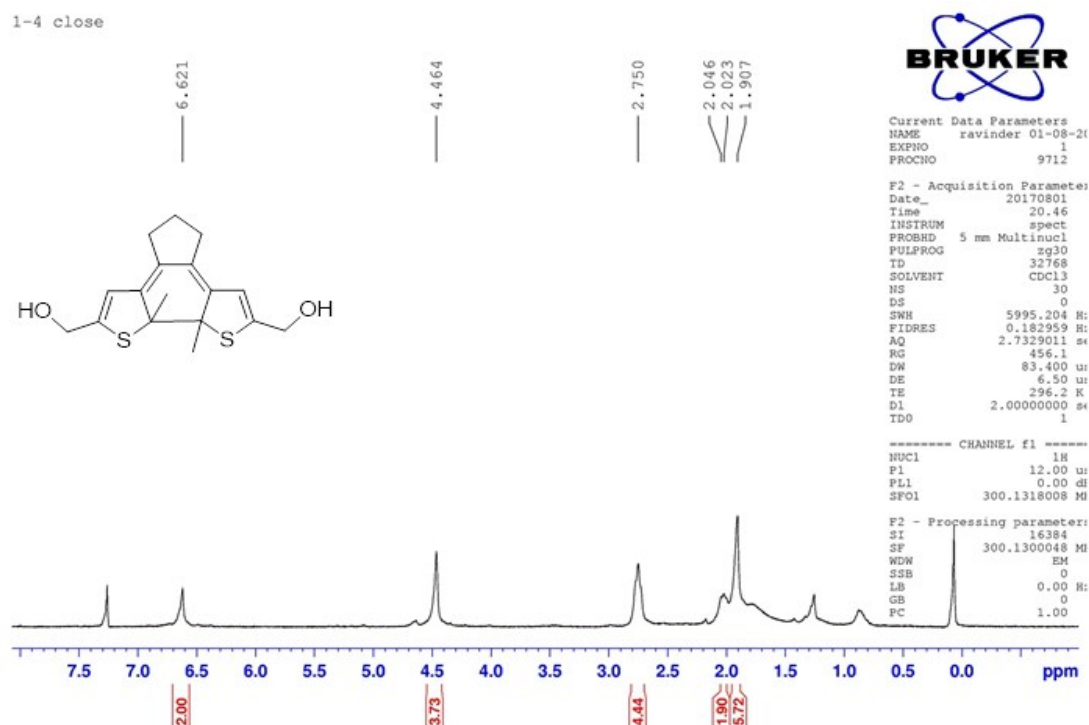


Fig. S18 ¹H-NMR of intermediate 1-4 (close).

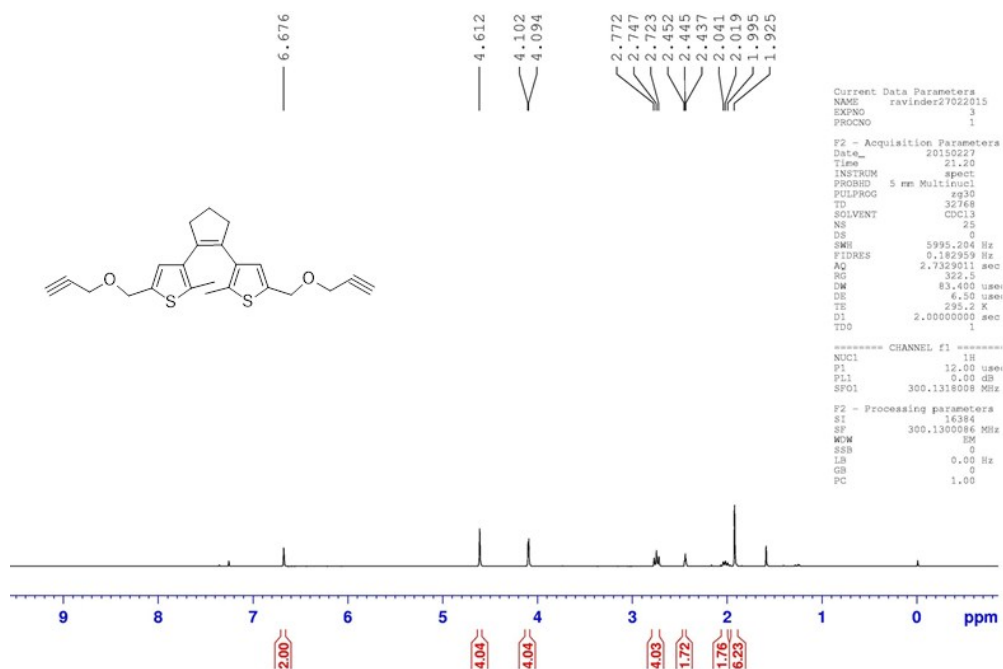


Fig. S19.1 ¹H-NMR of intermediate 1-5.

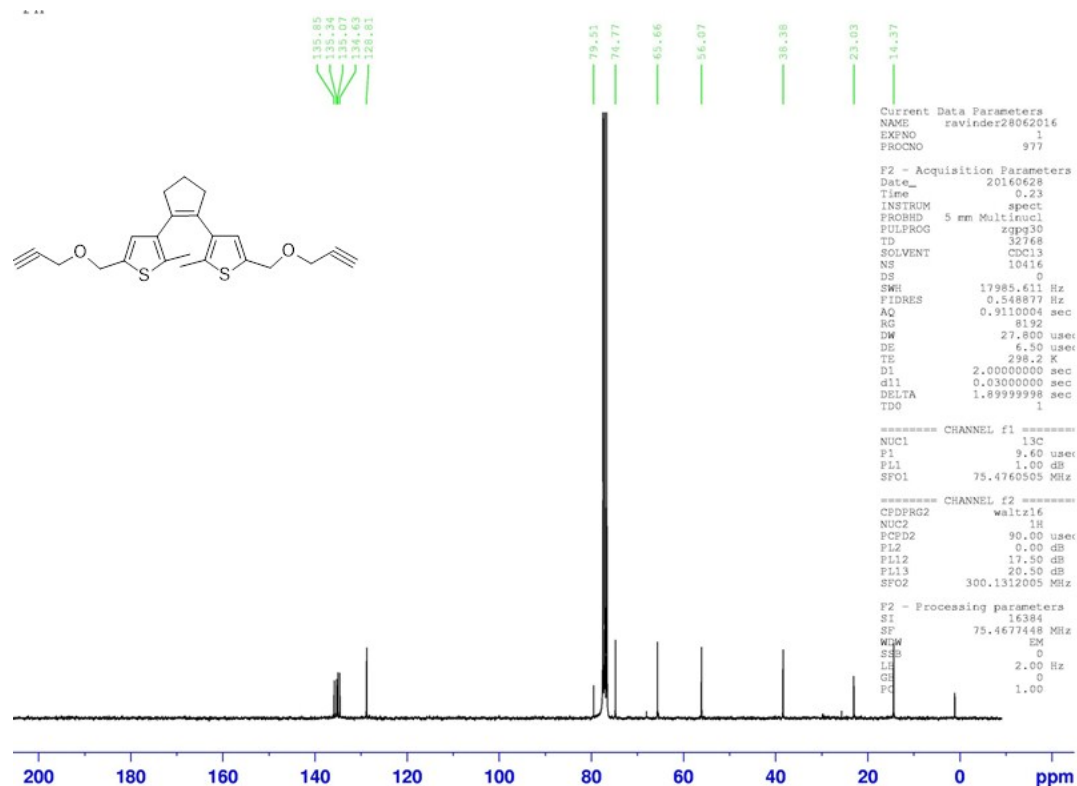


Fig. S19.2 ¹³C-NMR of intermediate 1-5.

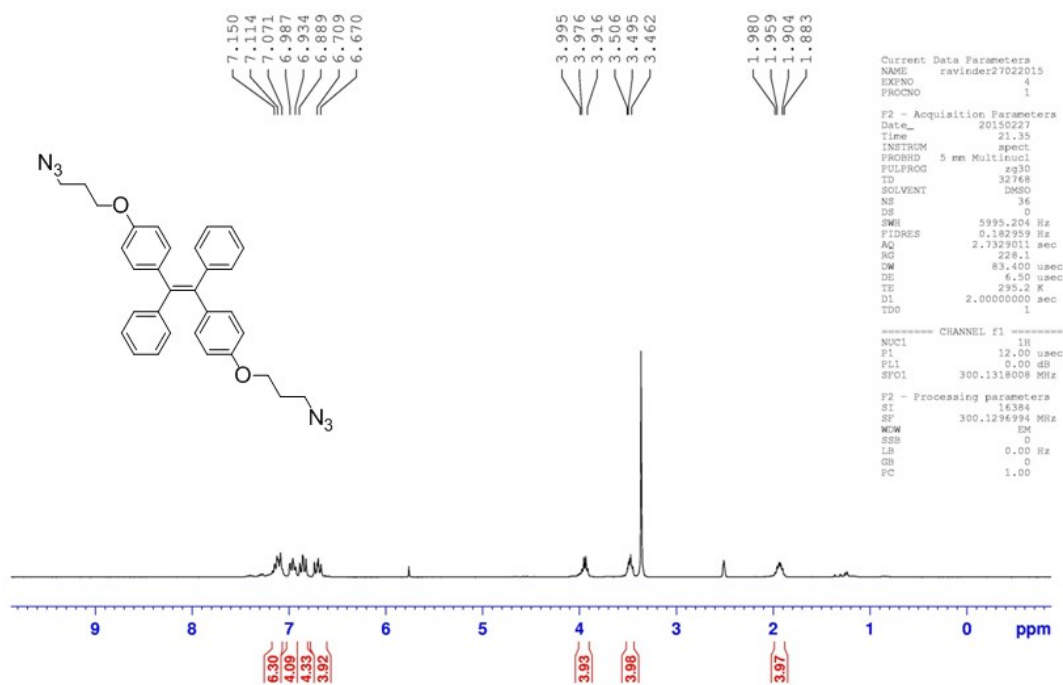


Fig. S20.1 ¹H-NMR of intermediate 2-3.

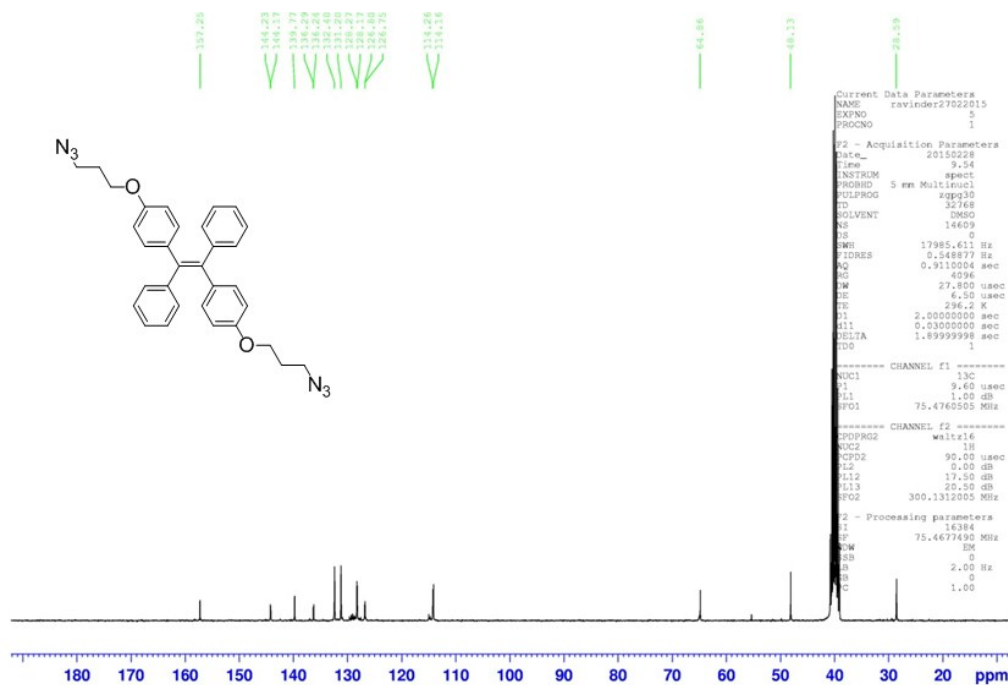


Fig. S20.2 ¹³C-NMR of intermediate 2-3.

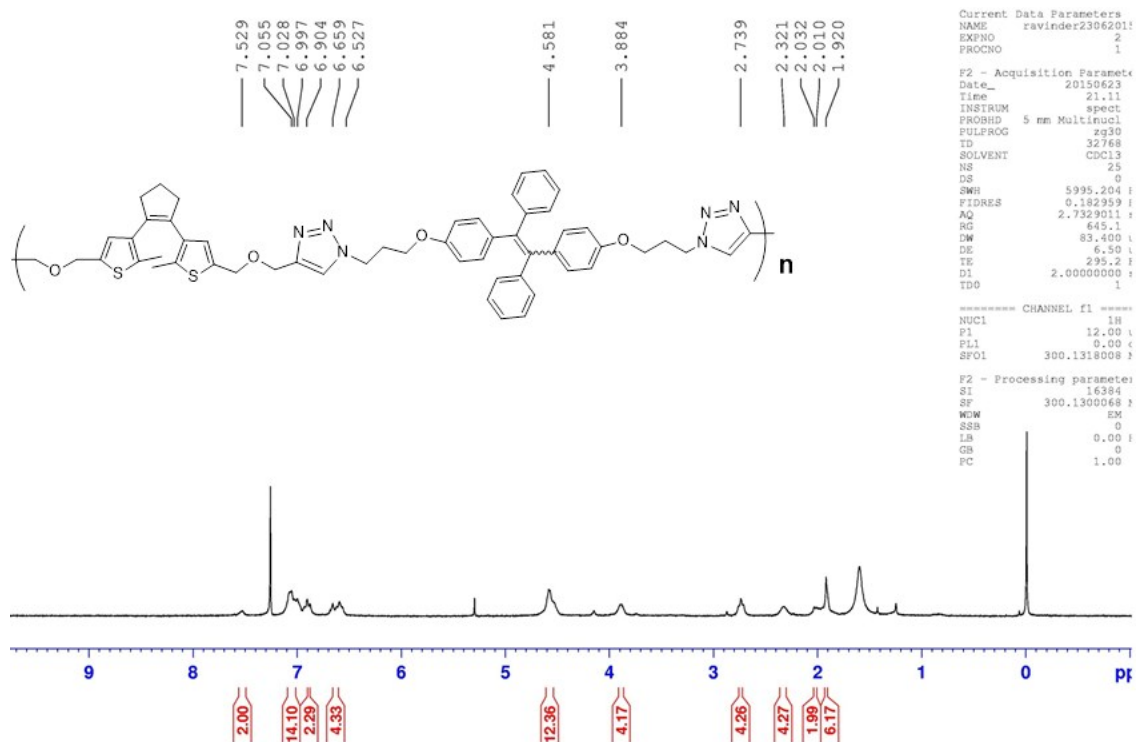


Fig. S21.1 ¹H-NMR of P-PHT.

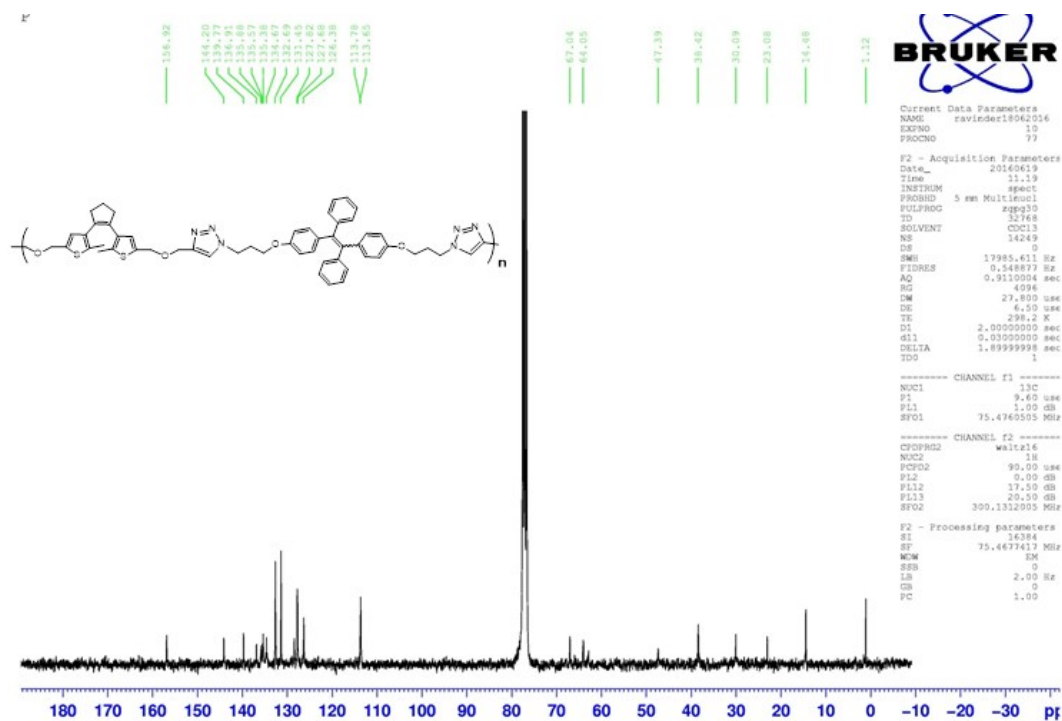


Fig. S21.2 ^{13}C -NMR of P-PHT.

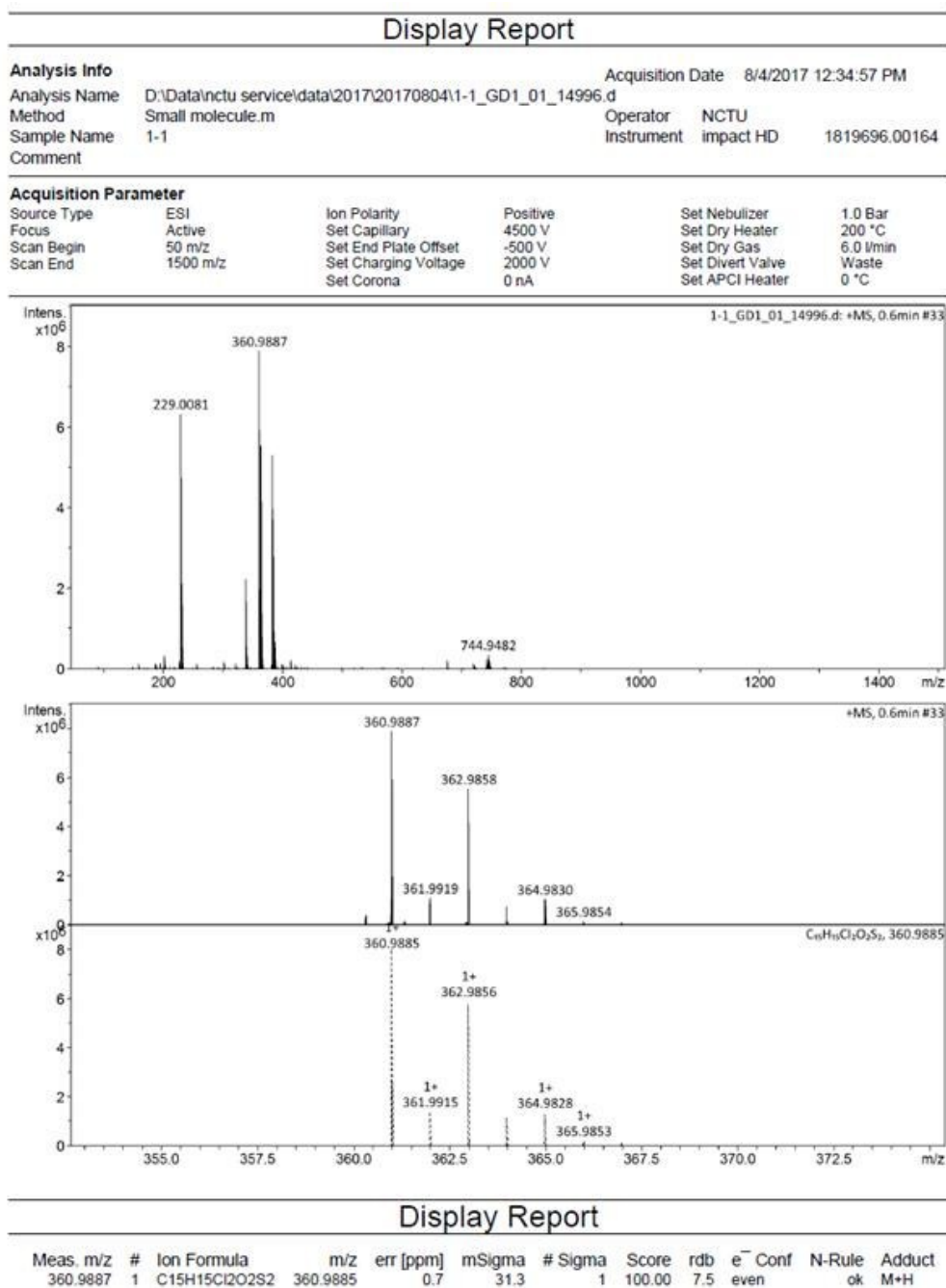


Fig. S22 HRMS (ESI) data of intermediate **1-1**.

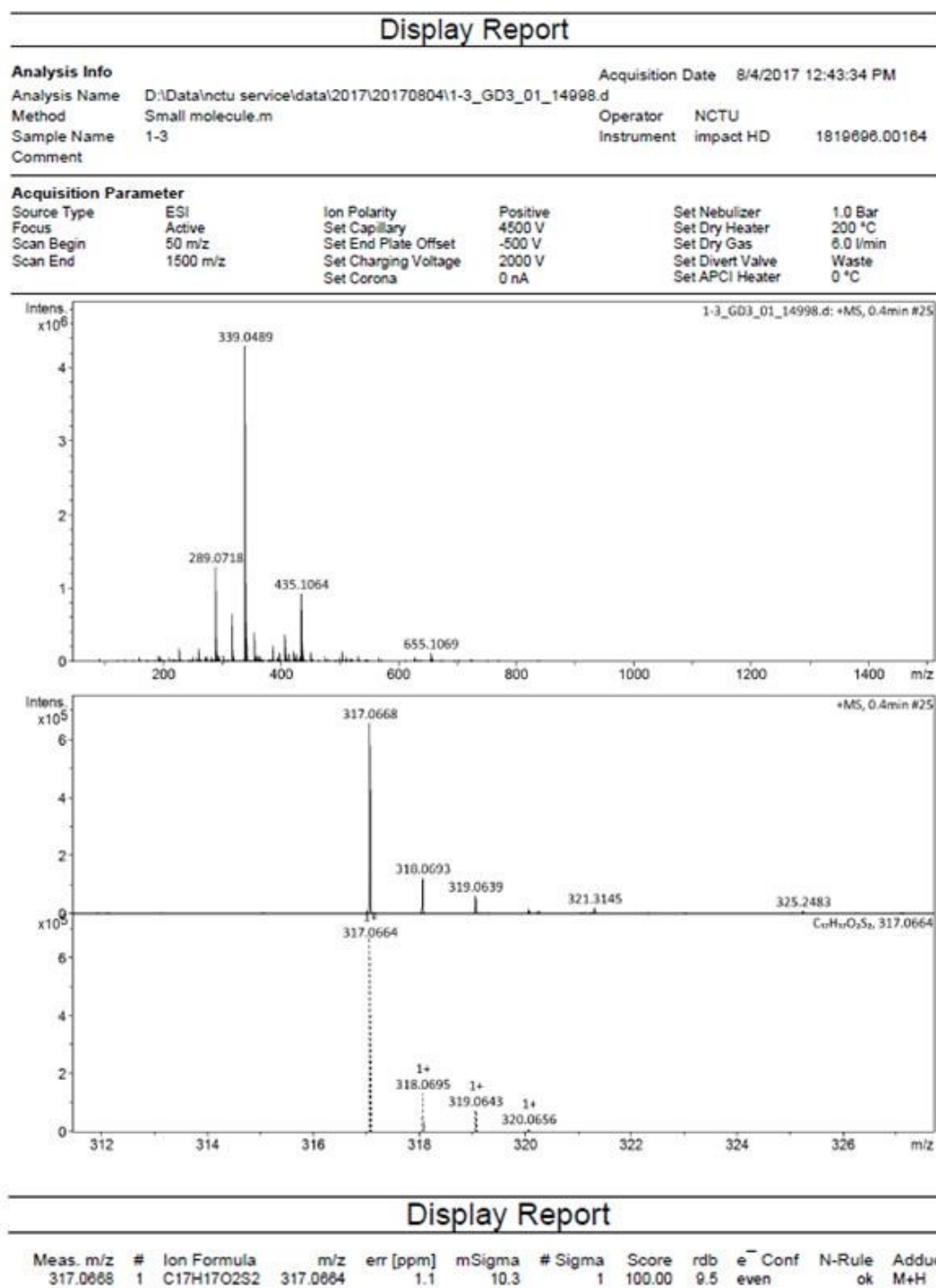


Fig. S23 HRMS (ESI) data of intermediate **1-3**.

Display Report

Analysis Info

Analysis Name	D:\Data\inctu service\data\2015\20151106\TPE-di-N3 ESI+_GA8_01_7912.d
Method	Small molecule.m
Sample Name	TPE-di-N3 ESI+
Comment	

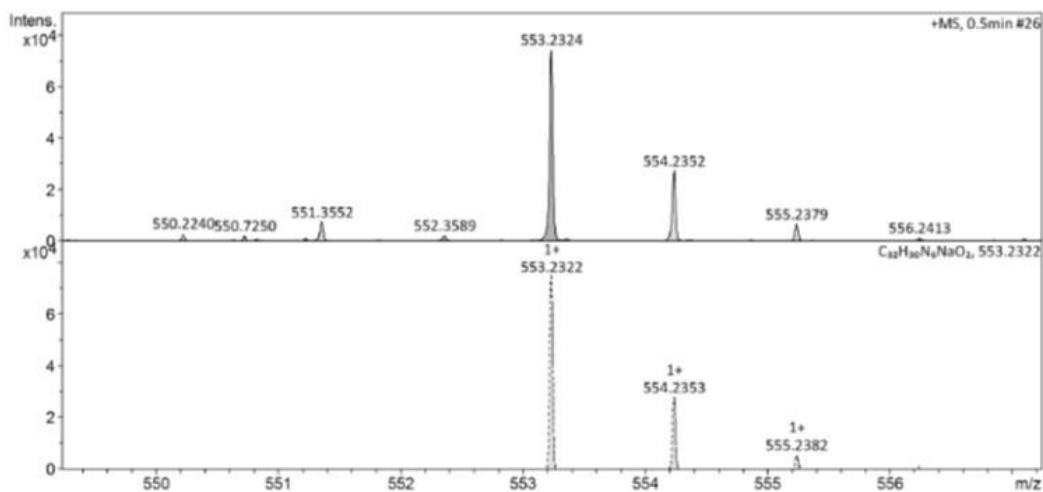
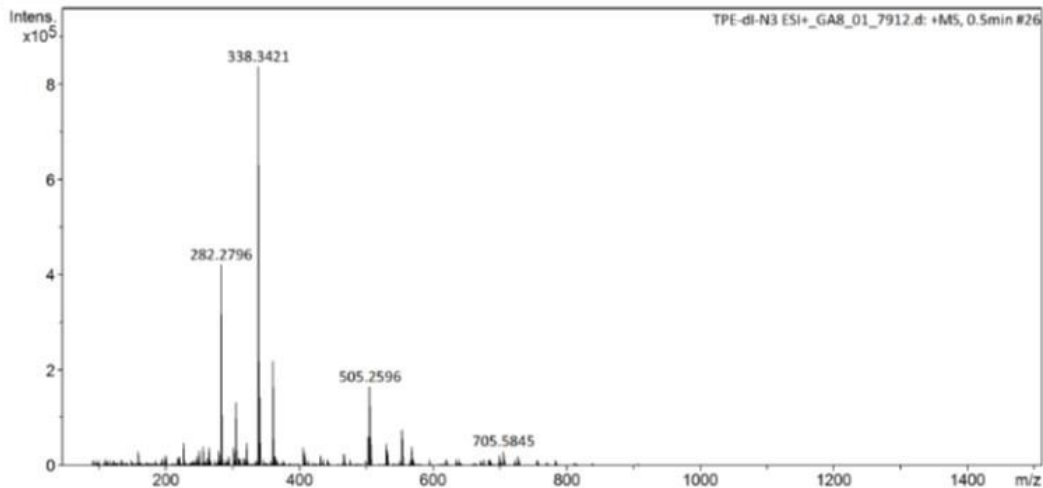
Acquisition Date 11/6/2015 2:16:21 PM

Operator NCTU

Instrument impact HD 1819696.00164

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive
Focus	Active	Set Capillary	4500 V
Scan Begin	50 m/z	Set End Plate Offset	-500 V
Scan End	1500 m/z	Set Charging Voltage	2000 V
		Set Corona	0 nA
		Set Nebulizer	1.0 Bar
		Set Dry Heater	200 °C
		Set Dry Gas	6.0 l/min
		Set Divert Valve	Waste
		Set APCI Heater	0 °C



Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e ⁻ Conf	N-Rule	Adduct
553.2324	1	C32H30N6NaO2	553.2322	0.2	9.3	1	100.00	20.5	even	ok	M+Na

Fig. S24 HRMS (ESI) data of intermediate **2-3**.

Display Report

Analysis Info

Analysis Name	D:\Data\ncu service\data\2016\20160902\Intermediate 1-5_BA4_01_10899.d
Method	Small molecule.m
Sample Name	Intermediate 1-5
Comment	

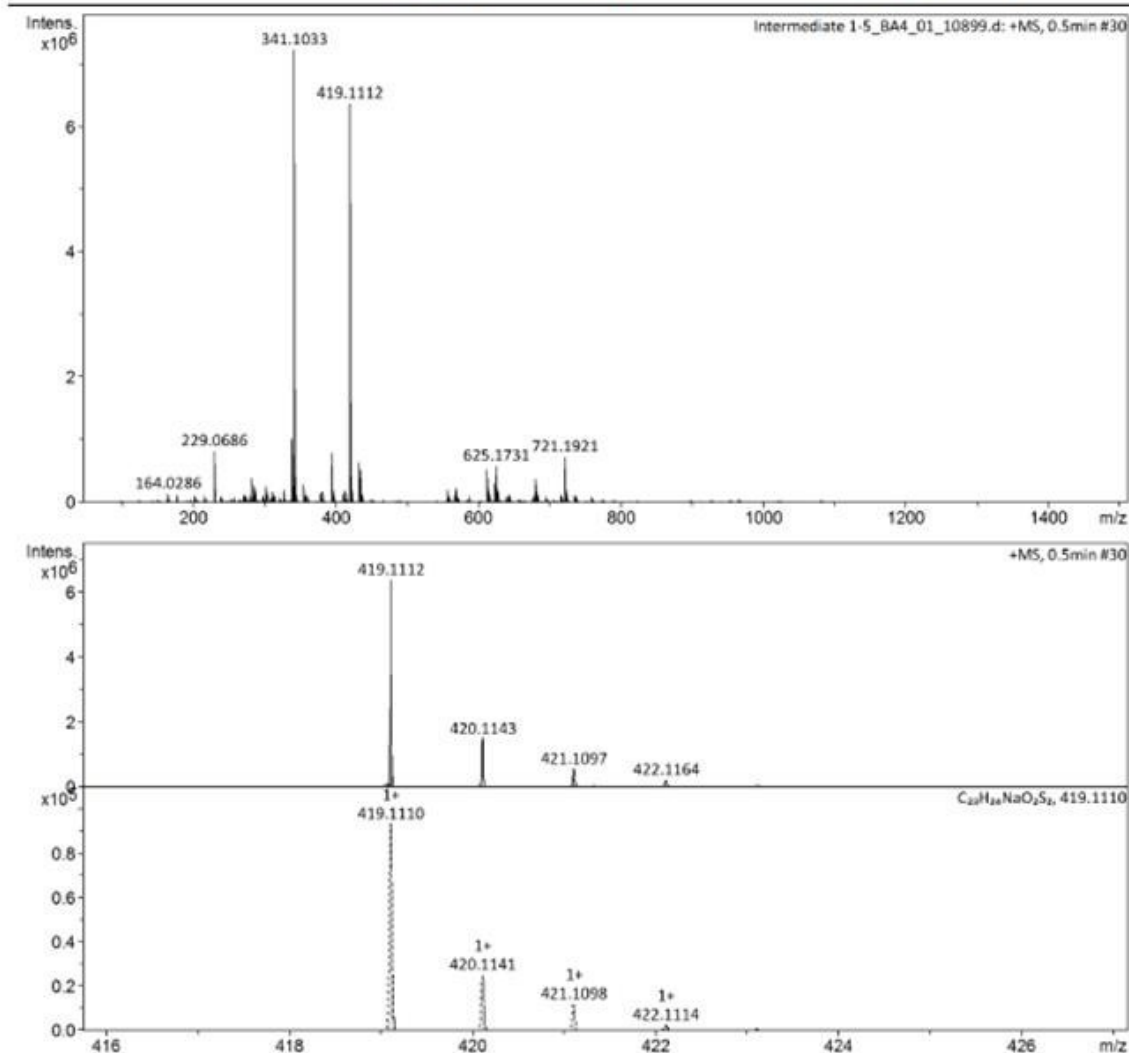
Acquisition Date 9/2/2016 10:23:48 AM

Operator NCTU

Instrument impact HD 1819696.00164

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive
Focus	Active	Set Capillary	4500 V
Scan Begin	50 m/z	Set End Plate Offset	-500 V
Scan End	1500 m/z	Set Charging Voltage	2000 V
		Set Corona	0 nA
		Set Nebulizer	1.0 Bar
		Set Dry Heater	200 °C
		Set Dry Gas	6.0 l/min
		Set Divert Valve	Waste
		Set APCI Heater	0 °C



Display Report

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e ⁻ Conf	N-Rule	Adduct
419.1112	1	C ₂₃ H ₂₄ NaO ₂ S ₂	419.1110	0.5	24.5	1	100.00	11.5	even	ok	M+Na

Fig. S25 HRMS (ESI) data of intermediate 1-5.

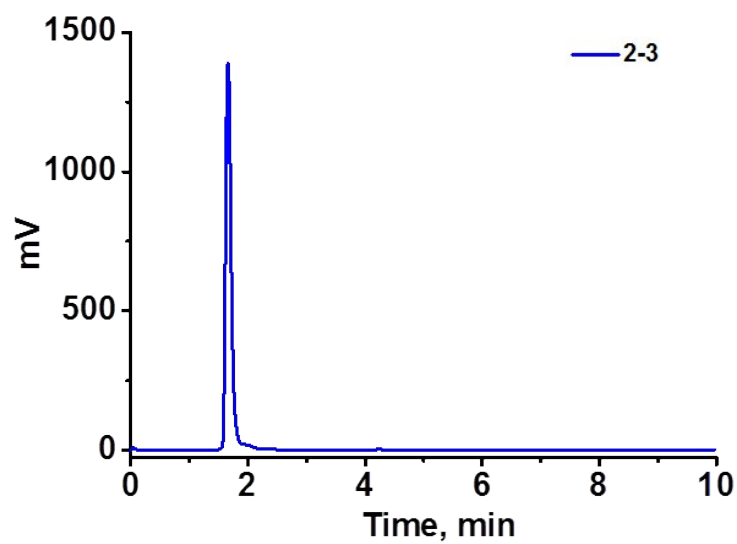


Fig. S26 HPLC of intermediate **2-3** in ethyl acetate (EA) solvent. (Retention time of peak = 1.65 min).

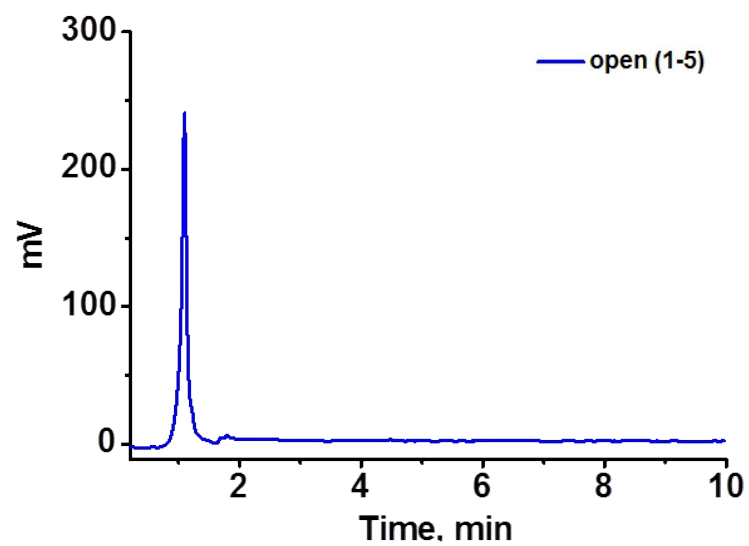


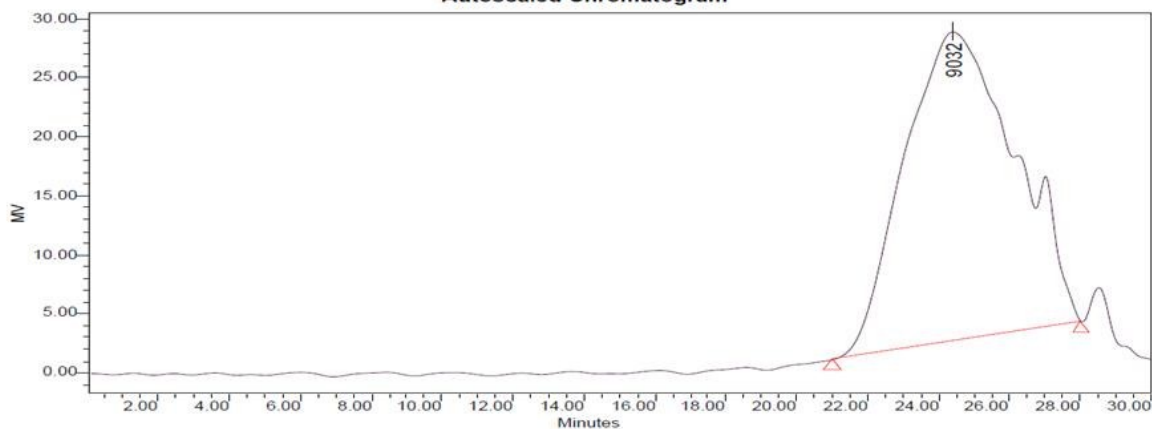
Fig. S27 HPLC of intermediate **1-5** in ethyl acetate (EA) solvent. (Retention time of peak = 1.09 min).

SAMPLE INFORMATION

Sample Name: Unk
Sample Type: Broad Unknown
Vial: 1
Injection #: 1
Injection Volume: 200.00 μ l
Run Time: 30.00 Minutes

Acquired By: System
Date Acquired: 2015/7/10 10:42:57
Acq. Method: THF_40_1
Date Processed: 2015/7/10 11:26:40
Channel Name: 410
Sample Set Name: 20150710_min

Autoscaled Chromatogram



GPC Results

Dist Name	Elution Volume (ml)	Retention Time (min)	Adjusted RT (min)	Mn	Mw	MP	Mz	Mz+1	Mz/Mw	Mz+1/Mw
1	24.373	24.373	24.373	7489	11634	9032	17858	24751	1.534973	2.127512

GPC Results

Area (sec)	% Area	Height ()	% Height	Integration Type	Peak Codes	Points Across Peak	Start Time (min)	End Time (min)	Baseline Start (min)
5688572	100.00	26213	100.00	bb		420	21.000	28.000	21.000

GPC Results

Baseline End (min)	Slope (/sec)	Offset ()
1 28.000	4.613982e-001	-8.495745e+000

Fig. S28 GPC data of P-PHT.