Supporting Information

Synthesis and photovoltaic properties of narrow band gap copolymers of dithieno[3, 2-*b*:2',3'-*d*]thiophene and diketopyrrolopyrrole

Abasaheb V. Patil[a], Woo –Hyung Lee[b], Kyuri Kim[a], Hanok Park [a], In Nam Kang [b,]*, Soo-Hyoung Lee [a,]*

[a] School of Semiconductor and Chemical Engineering, Chonbuk National University, Duckjin-dong 664-14, Jeonju 561- 756, Republic of Korea.

[b] Department of Chemistry, The Catholic University, 43-1, Yeokaok2-dong, Wonmi-gu, Buchen-si, Gyeonggi-do 420-743, Republic of Korea.

Email: * shlee66@jbnu.ac.kr; inamkang@catholic.ac.kr

Contents

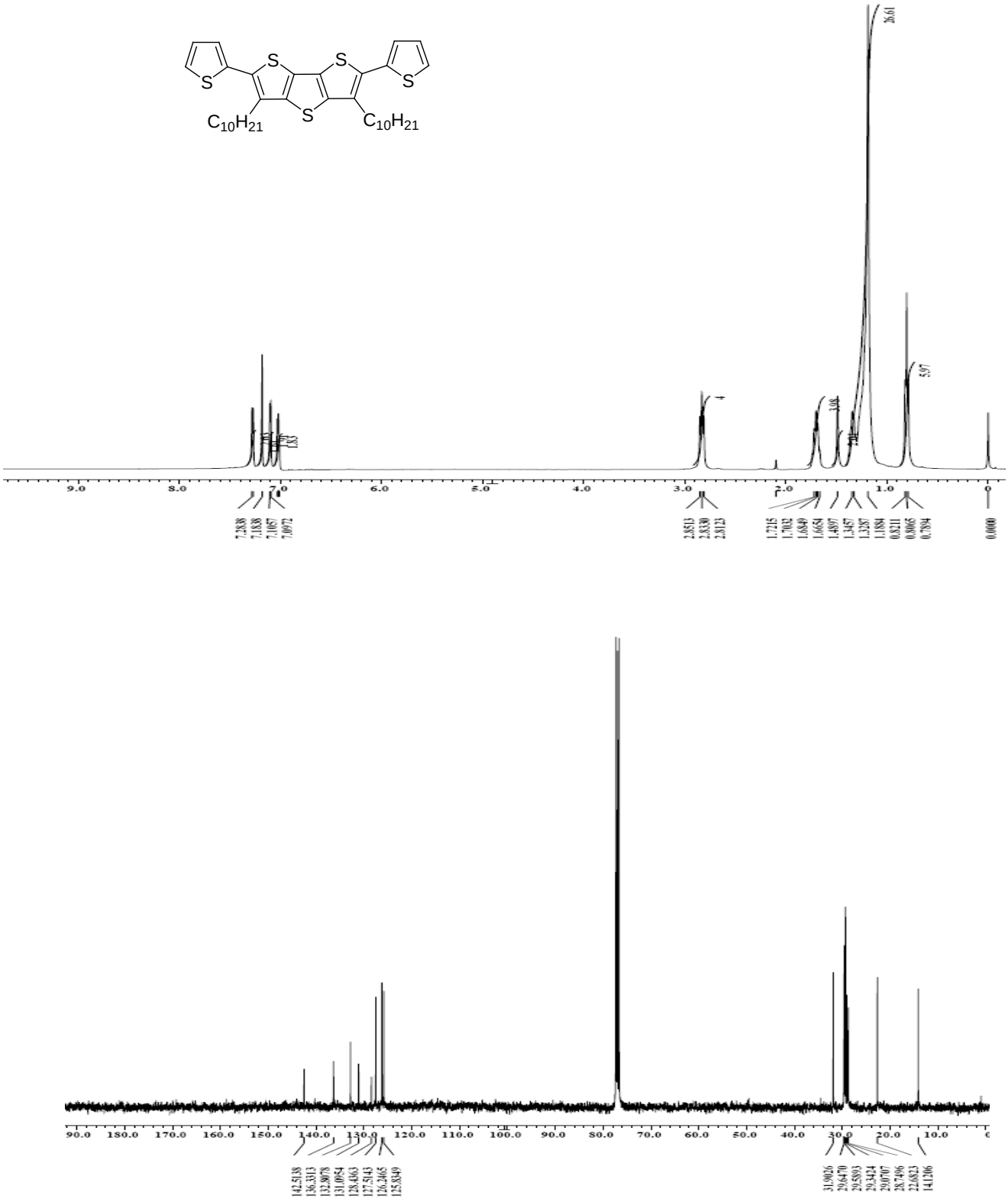

Figure S1. ^{1}H and ^{13}NMR spectra of compound **4**.

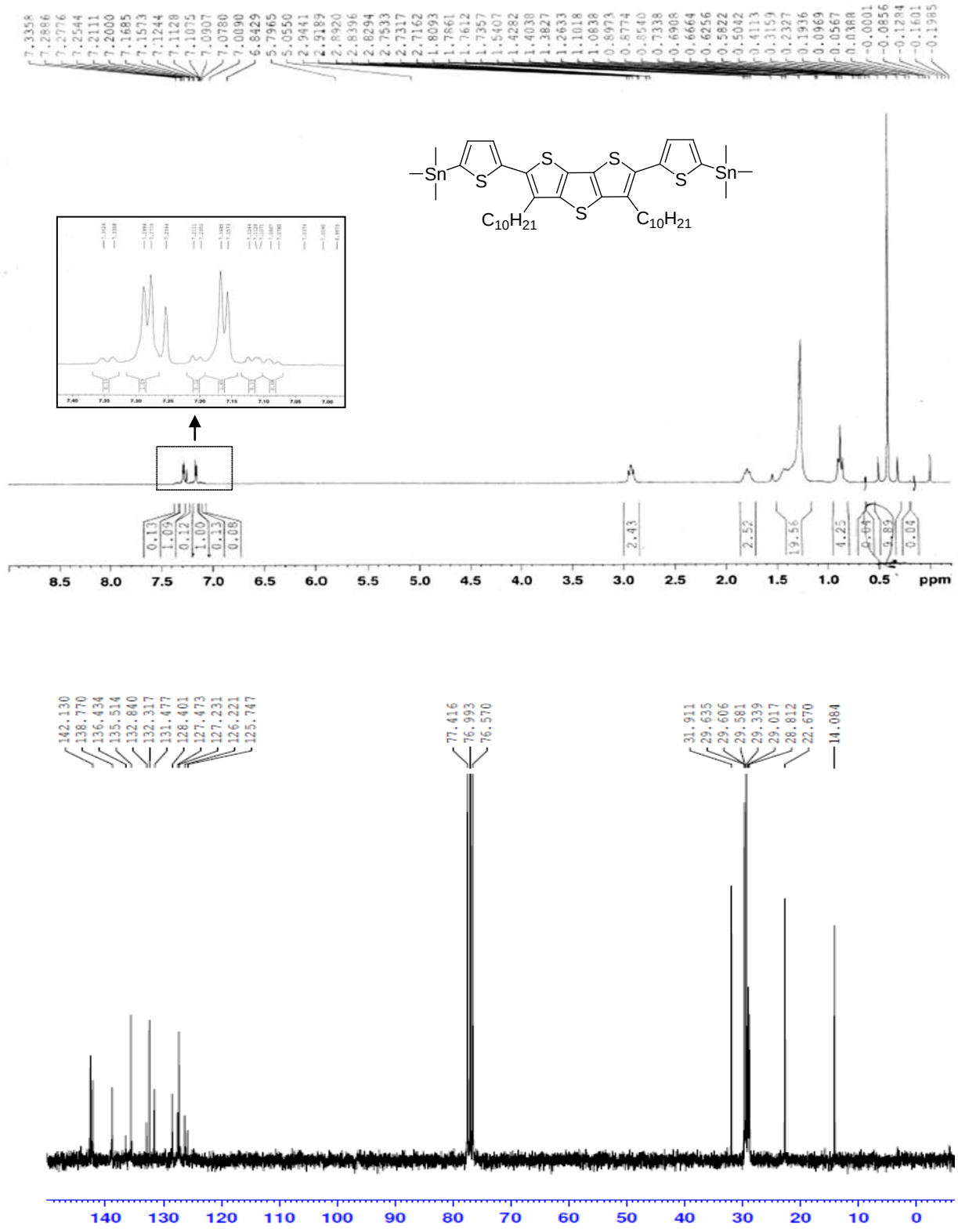

Figure S2. ^{1}H and ^{13}C NMR spectra of compound **5**.

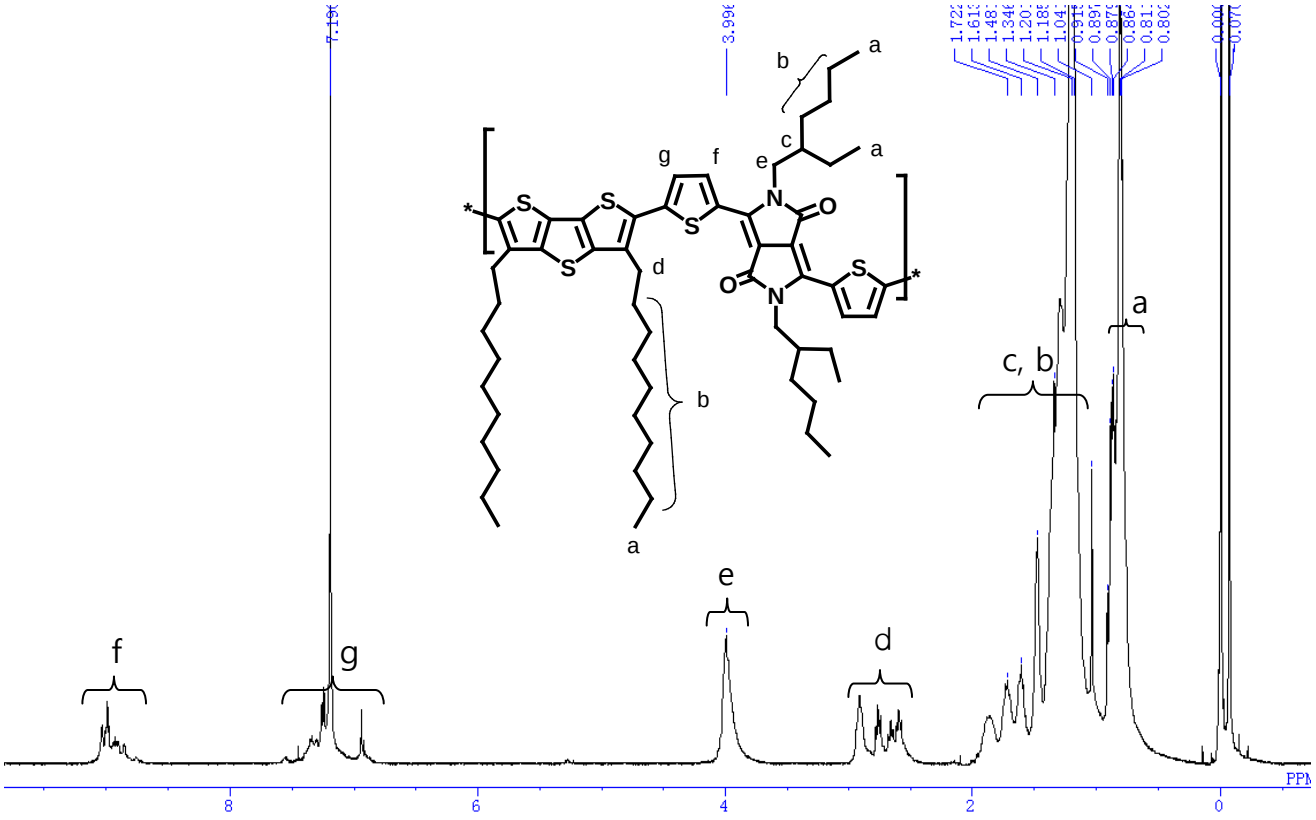

Figure S3. ^{1}H NMR spectrum of **PDTTDPP** copolymer in $CDCl_3$.

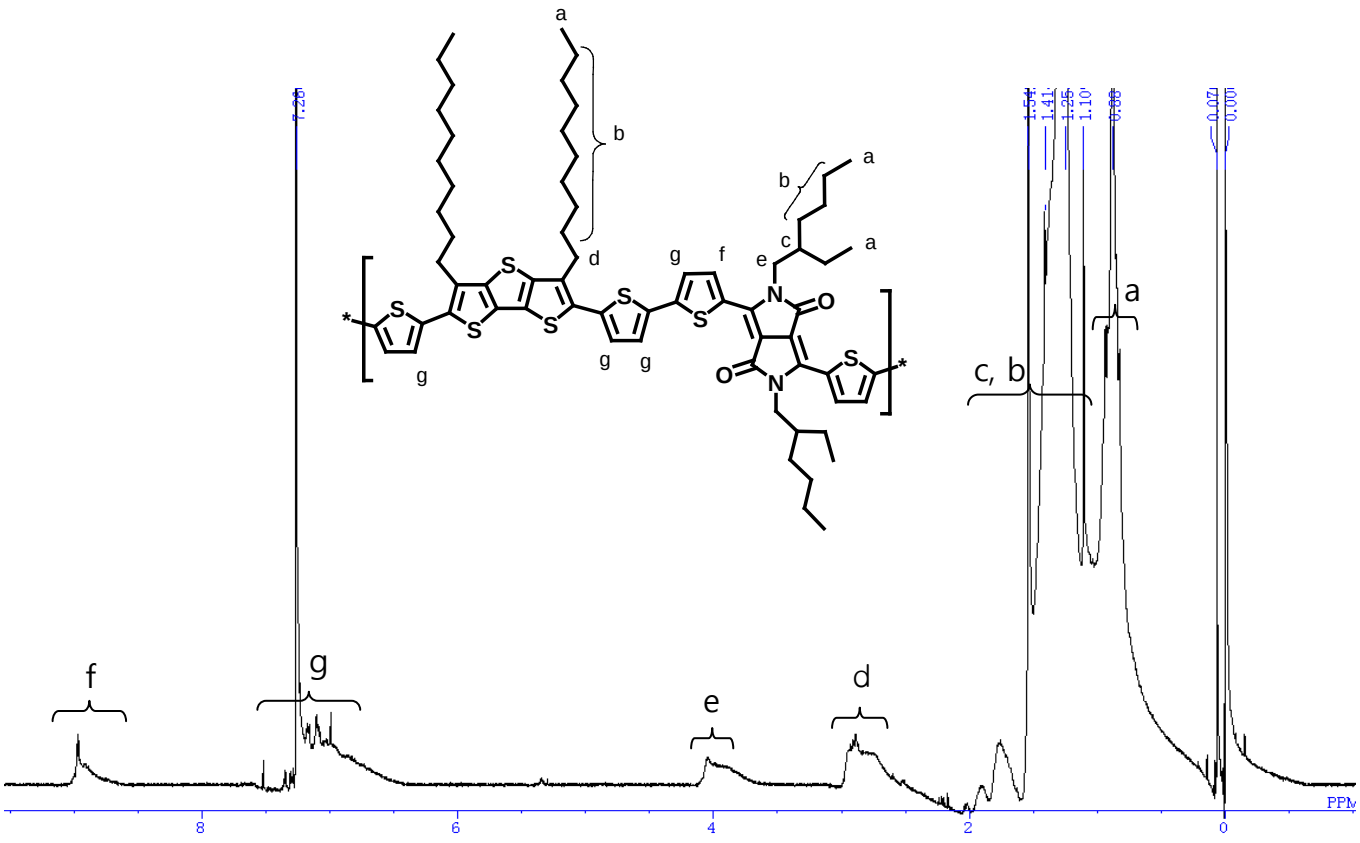

Figure S4. ^{1}H NMR spectrum of **PTDTTTDPP** copolymer in $CDCl_3$.

We measured molecular weights of PDTTDPP and PTDTTTDPP by Maldi-TOF-mass method and another GPC system to confirm their real values. As shown in Table S1, molecular weight shows consistent values with different measurements.

Table S1. Molecular weights of copolymers PDTTDPP and PTDTTTDPP by different measurements.

Polymers	GPC 1 (data in manuscript) (Model: Futecs NP-4000, Column: Shodex LF-804)			GPC 2 (Model: Waters 1515, Column: Shodex LF-804 X3)			Maldi-TOF-mass (Model: Voyager-DE STR, Applied Biosystems)		
	M_n (g mol^{-1})	M_w (g mol^{-1})	PDI	M_n (g mol^{-1})	M_w (g mol^{-1})	PDI	M_n (g mol^{-1})	M_w (g mol^{-1})	PDI
PDTTDPP	5,215	5,730	1.09	5,727	6,458	1.13	4,404.4	5,058.7	1.15
PTDTTTDPP	5,516	9,995	1.81	5,866	10,996	1.87	4,551.8	5,553.1	1.22

Further studies currently being pursued in our laboratory to improve the solar cell performances of these copolymers (1) by polymer structural modification to improve their solubility and molecular weight by adding longer alkyl chains in the DPP unit, (2) by optimization of device fabrication conditions based on device physics (e.g., using co-solvent, thermal annealing and processing additives). One of preliminary device optimization works using thermal annealing of devices with temperature of 90 ^{o} C for 20 min is shown in Table S2. In this condition, thermal annealing gave poorer device performances except PTDTTTDPP:$PC_{61}BM$ (1:2) device. More studies are in progress with testing the devices with different temperatures and time, with also other device fabrication conditions (co-solvent, and processing additives, etc).

Table S2. Photovoltaic properties of polymer solar cell devices based on the copolymers PDTTDPP and PTDTTTDPP with thermal annealing (90 ^{o} C for 20 min).

Polymer (ratio with $PC_{61}BM$)	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	PCE (%)
PDTTDPP (1:1)	1.47	0.65	0.31	0.29
PDTTDPP (1:1) annealing	0.77	0.67	0.25	0.13
PTDTTTDPP (1:1)	5.15	0.60	0.45	1.39
PTDTTTDPP (1:1) annealing	3.47	0.60	0.28	0.59
PTDTTTDPP (1:2)	2.67	0.57	0.24	0.36
PTDTTTDPP (1:2) annealing	3.44	0.59	0.37	0.75
PTDTTTDPP (1:4)	2.76	0.54	0.57	0.85
PTDTTTDPP (1:4) annealing	2.63	0.56	0.56	0.82

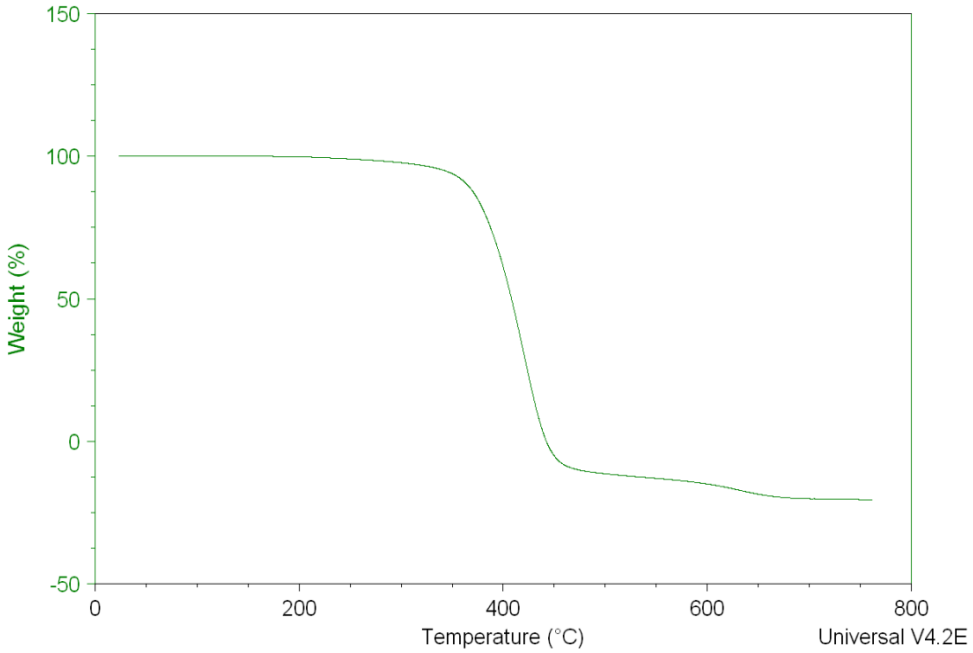

Figure S5. TGA curve of PDTTDPP with a heating rate of 20˚C/min.

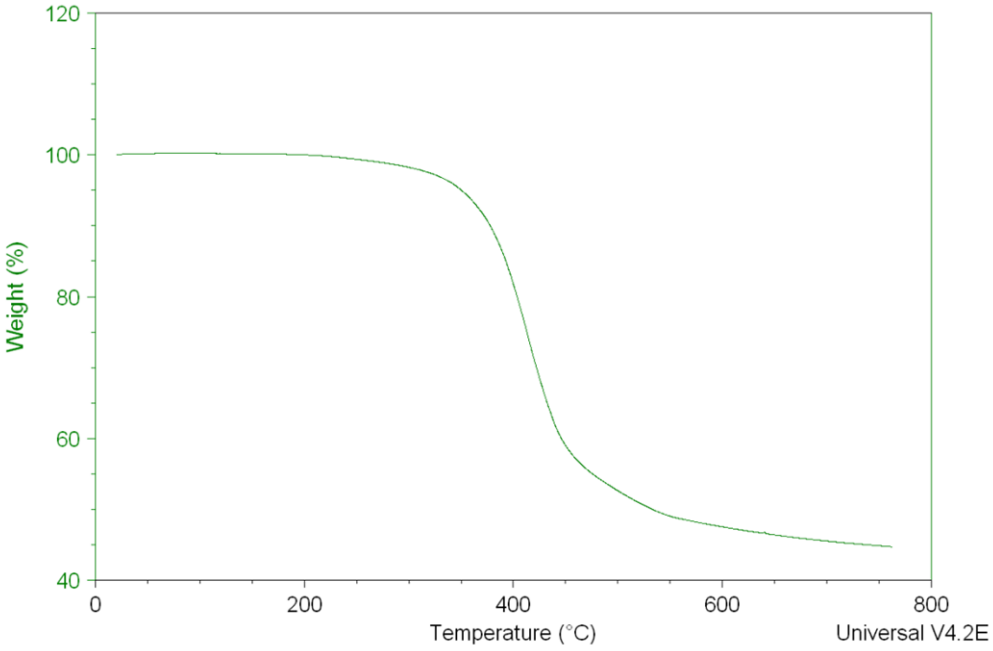

Figure S6. TGA curve of **PTDTTTDPP** with a heating rate of 20˚C/min.