Electronic Supporting Information for

Simple Molecular Structure of *ortho*-Derived Perylene Diimides Diploid for Non-Fullerene Organic Solar Cells with Efficiency over 8%

Helin Wang, Lingcheng Chen* and Yi Xiao*

State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116024, China
lcchen@dlut.edu.cn; xiaoyi@dlut.edu.cn

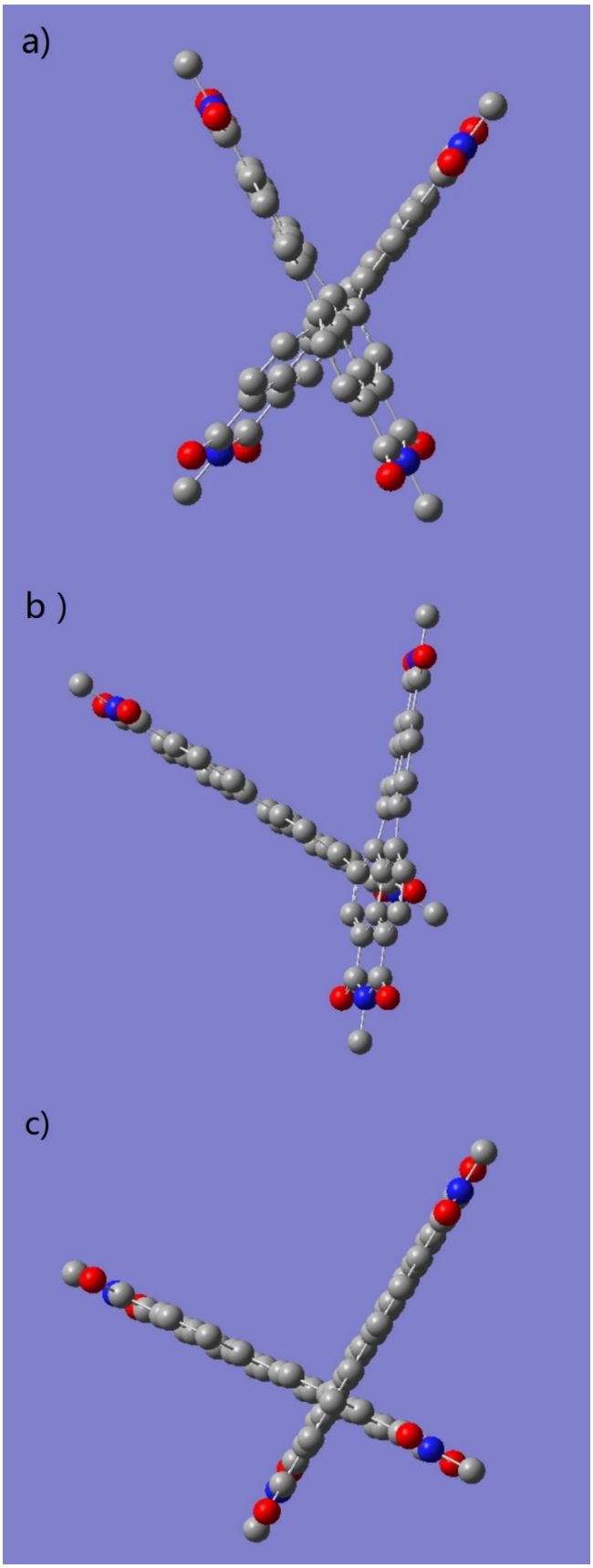

Fig. S1 Ground-state geometries of ***bb*-2PDI** (a), ***bo*-2PDI** (b), and ***oo*-2PDI** (c) calculated from density functional theory.

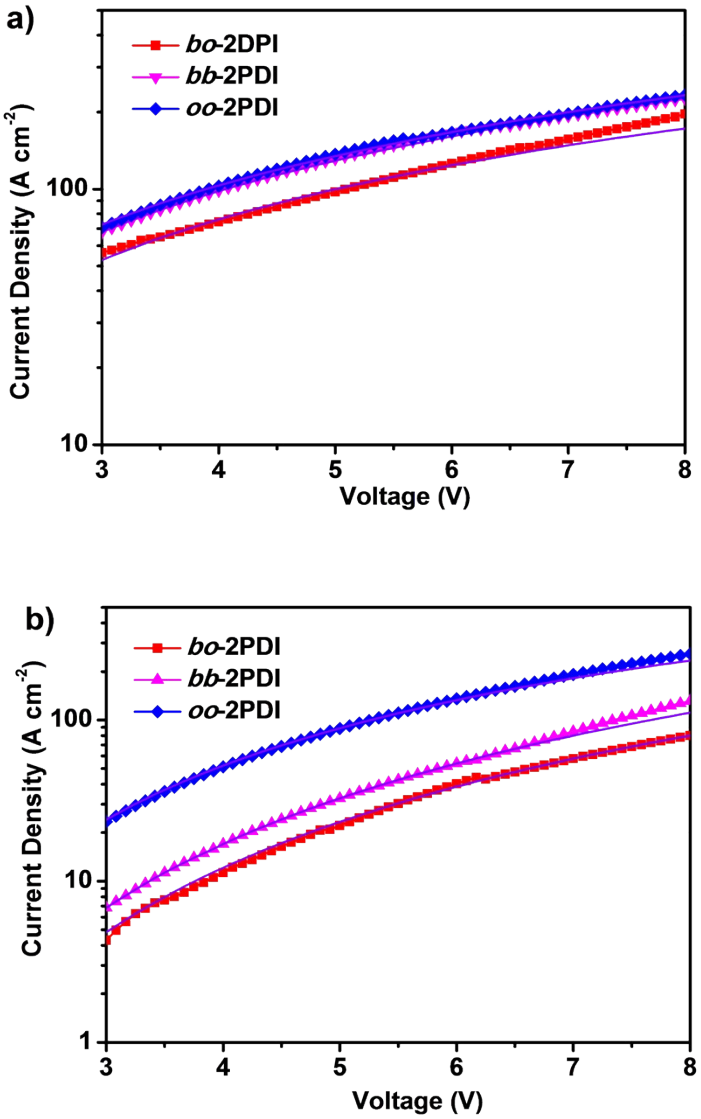

Fig. S2 The experimental current density-applied voltage (*J-V*) characteristics for a) hole-only devices, and b) electron-only devices for three kinds of blend films. The dot lines are measured value, and the violet lines are the theoretical fitting values.

Table S1. Summary of device parameters of **PTB7-Th**:***bb*-2PDI** solar cells

D/A [weight ratio]	Additives [by volume]	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF [%]	$PCE_{ave(max)}$ [%]
1.5:1		11.49±0.12 (11.61)	0.781±0.004 (0.784)	47.3±0.4 (47.6)	4.22±0.11 (4.33)
1:1	NULL	12.96±0.13 (13.09)	0.791±0.003 (0.794)	49.2±0.3 (49.4)	5.03±0.10 (5.13)
1:1.5		11.18±0.15 (11.32)	0.775±0.005 (0.780)	50.1±0.6 (50.7)	4.35±0.13 (4.48)
	0.5% DIO	13.31±0.12 (13.42)	0.777±0.003 (0.780)	54.1±0.4 (54.5)	5.57±0.13 (5.70)
	1% DIO	16.59±0.11 (16.70)	0.778±0.002 (0.780)	48.9±0.3 (49.2)	6.31±0.10 (6.41)
	2% DIO	15.46±0.14 (15.60)	0.769±0.005 (0.774)	52.3±0.6 (52.8)	6.23±0.14 (6.37)
1:1	1% CN	12.13±0.14 (12.26)	0.756±0.004 (0.760)	53.0±0.3 (53.3)	4.86±0.11 (4.97)
	2% CN	11.84±0.12 (11.96)	0.778±0.004 (0.781)	52.0±0.5 (52.5)	4.78±0.12 (4.90)
	2% DPE	11.71±0.12 (11.82)	0.752±0.004 (0.756)	52.8±0.4 (53.2)	4.64±0.11 (4.75)
	4% DPE	11.49±0.13 (11.62)	0.748±0.005 (0.753)	52.8±0.3 (53.0)	4.51±0.13 (4.64)

Table S2. Summary of device parameters of **PTB7-Th**:***bo*-2PDI** solar cells

D/A [weight ratio]	Additives [by volume]	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF [%]	$PCE_{ave(max)}$ [%]
1.5:1		4.84±0.12 (4.95)	0.681±0.003 (0.683)	38.7±0.4 (39.1)	1.24±0.08 (1.32)
1:1	NULL	6.37±0.11 (6.47)	0.693±0.002 (0.695)	38.9±0.2 (39.1)	1.71±0.05 (1.76)
1:1.5		4.84±0.13 (4.97)	0.633±0.003 (0.635)	38.6±0.5 (39.1)	1.12±0.11 (1.23)
	0.5% DIO	6.07±0.13 (6.19)	0.681±0.003 (0.684)	38.2±0.5 (38.6)	1.51±0.12 (1.63)
	1% DIO	7.51±0.12 (7.63)	0.668±0.002 (0.669)	39.1±0.3 (39.3)	1.95±0.06 (2.01)
	2% DIO	6.16±0.14 (6.30)	0.668±0.003 (0.670)	36.9±0.3 (37.2)	1.48±0.09 (1.57)
1:1	1% CN	5.29±0.11 (5.40)	0.628±0.004 (0.631)	36.6±0.4 (37.0)	1.15±0.11 (1.26)
	2% CN	4.34±0.12 (4.45)	0.643±0.004 (0.647)	38.3±0.3 (38.1)	1.02±0.09 (1.11)
	2% DPE	4.23±0.13 (4.36)	0.627±0.005 (0.632)	40.2±0.3 (40.3)	1.03±0.08 (1.11)
	4% DPE	4.28±0.13 (4.41)	0.638±0.002 (0.639)	37.9±0.4 (38.3)	1.03±0.05 (1.08)

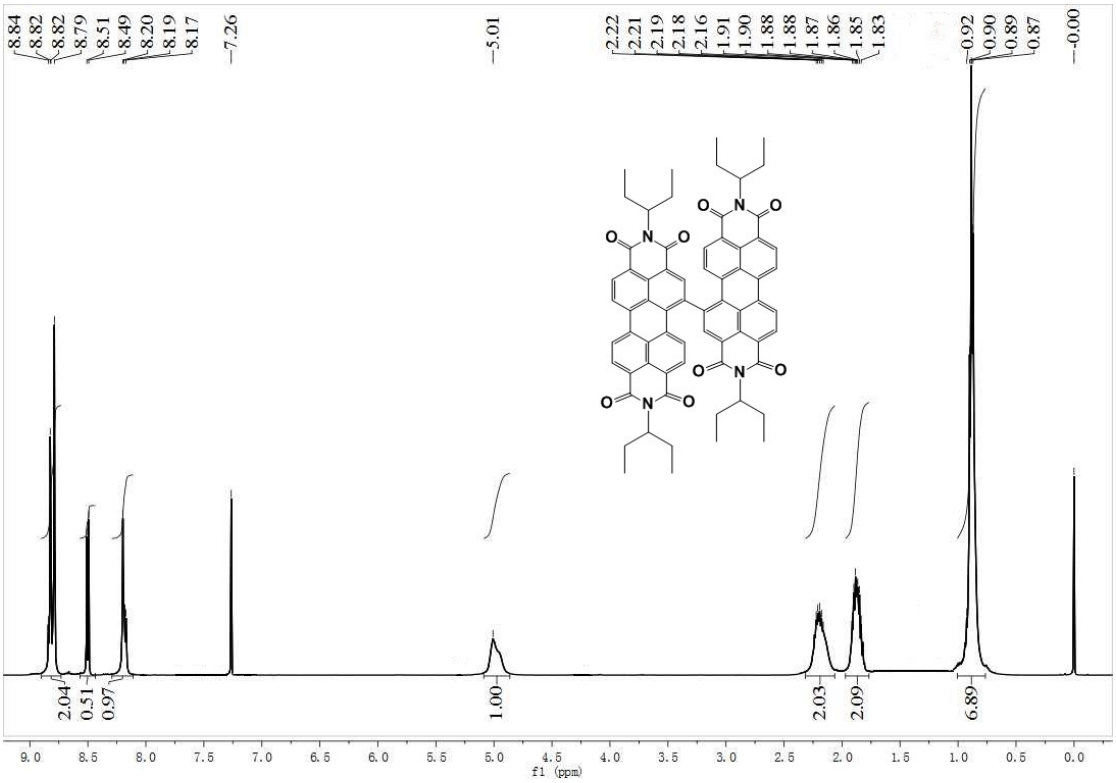

Fig. S3 ^{1}H-NMR of compound ***bb*-2PDI** in $CDCl_3$.

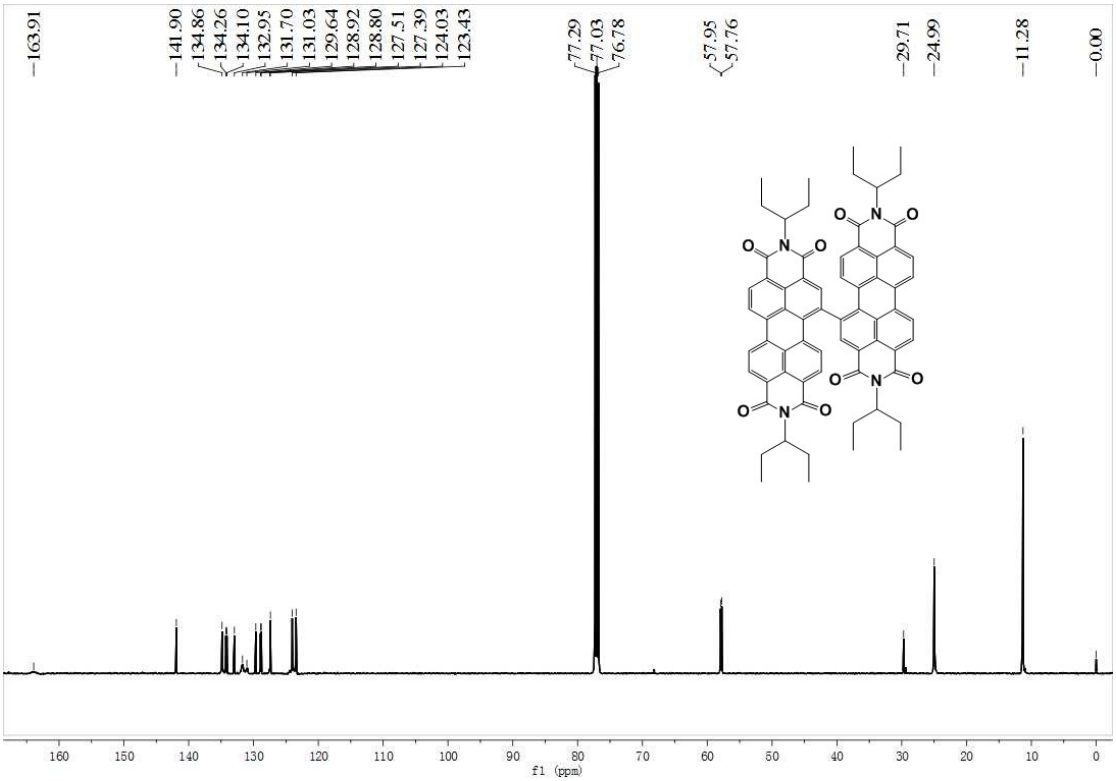

Fig. S4 ^{13}C-NMR of compound ***bb*-2PDI** in $CDCl_3$.

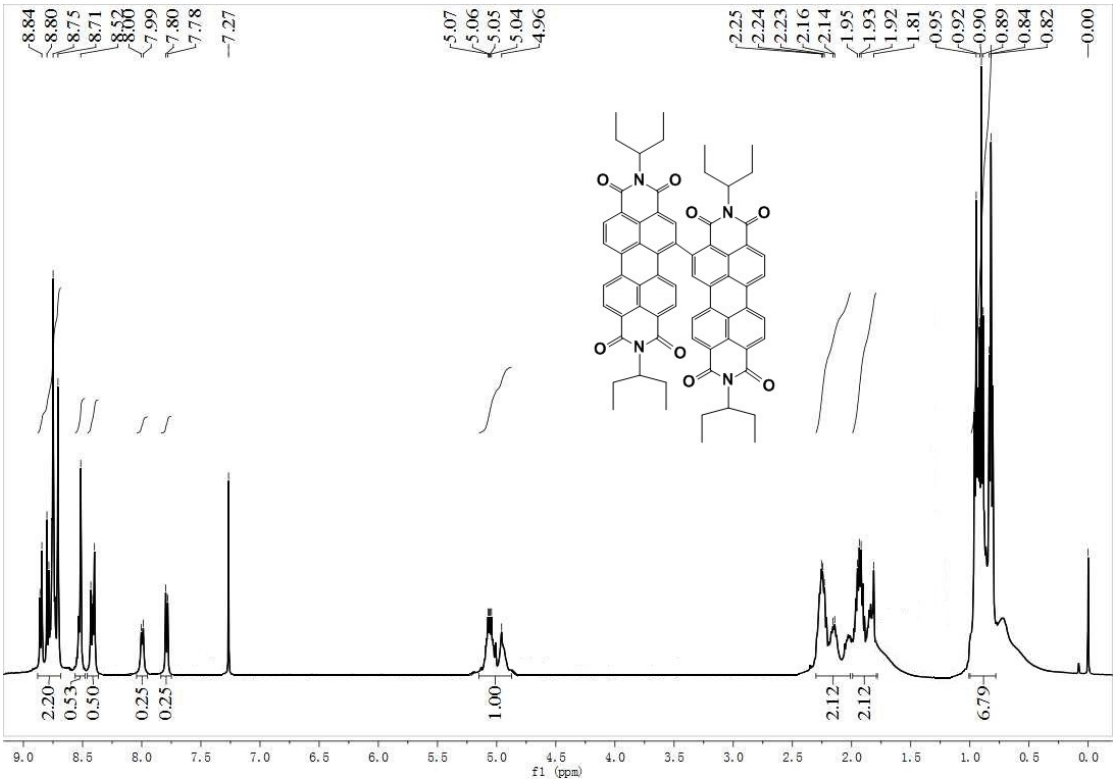

Fig. S5 ^{1}H-NMR of compound ***bo*-2PDI** in $CDCl_3$.

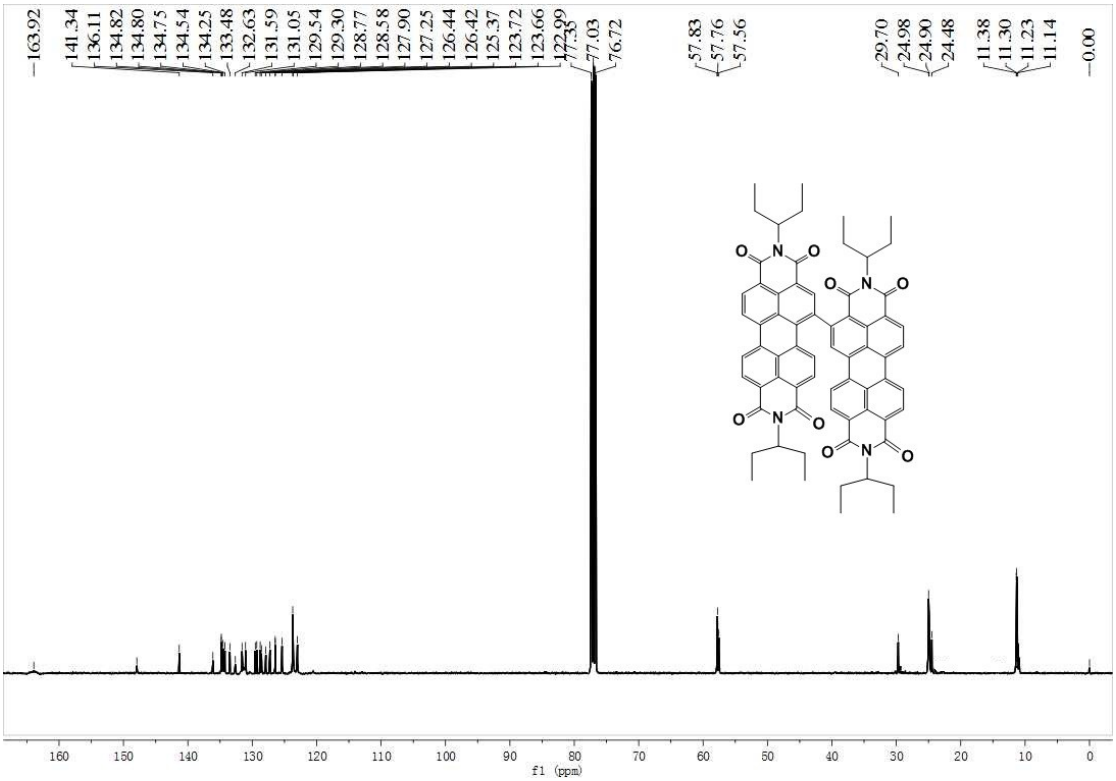

Fig. S6 ^{13}C-NMR of compound ***bo*-2PDI** in $CDCl_3$.

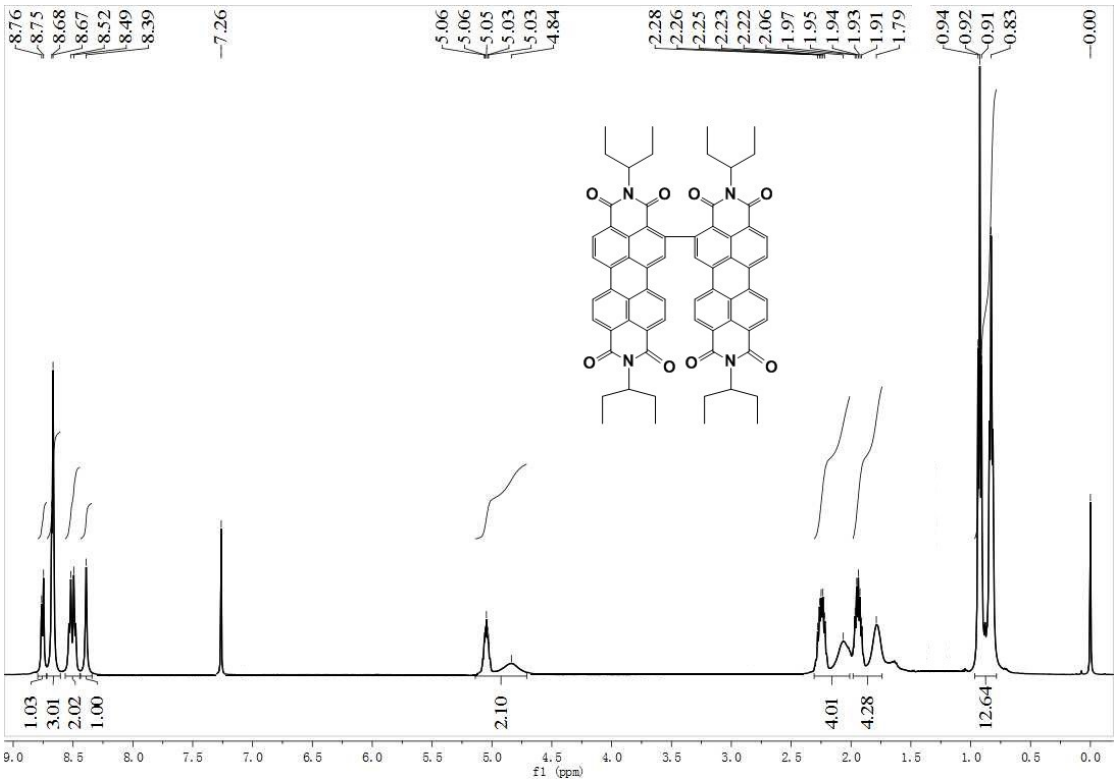

Fig. S7 ^{1}H-NMR of compound ***oo*-2PDI** in $CDCl_3$.

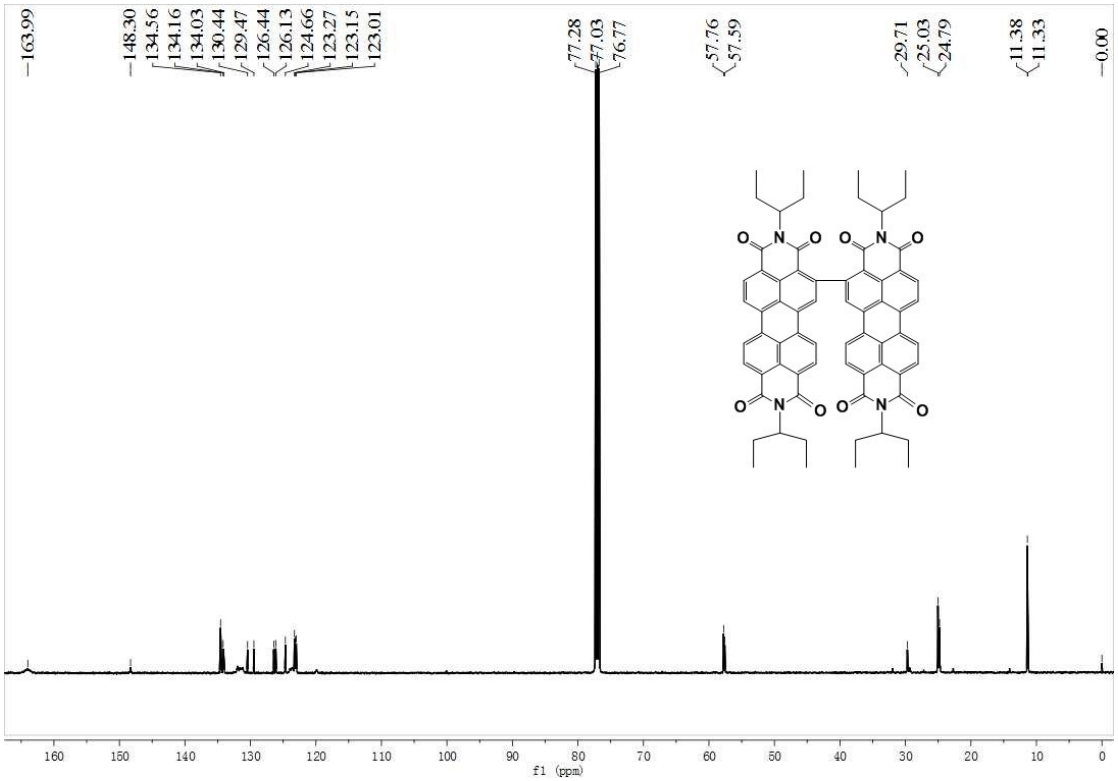

Fig. S8 ^{13}C-NMR of compound ***oo*-2PDI** in $CDCl_3$.