

Supplementary Information for

## Non-planar perylene-3,4,9,10-tetracarboxylic diimide acceptors with different geometrical linker units for efficient non-fullerene organic solar cells

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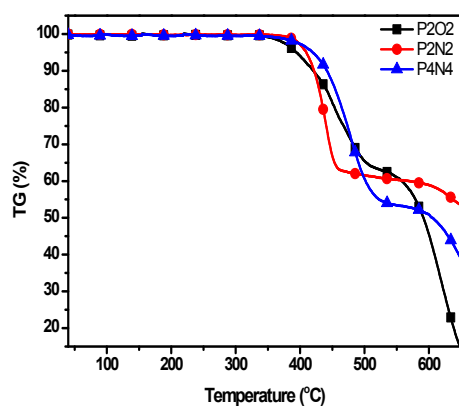


Fig. S1 The TG curve of the acceptors.

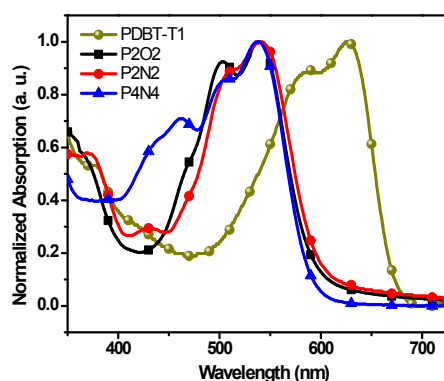
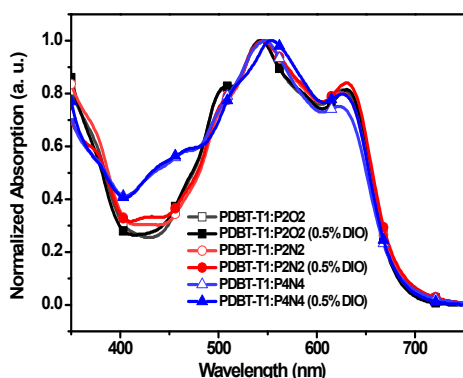
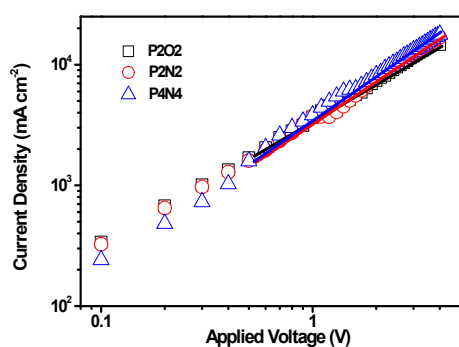


Fig. S2 UV-vis absorption spectra of the three PDI acceptors and PDBT-T1 in solid states.



**Fig. S3** UV-vis absorption spectra of the three PDI acceptors based blend films with/without DIO additive.



**Fig. S4** Current-voltage ( $I$ - $V$ ) characteristics of the PDIs neat films in space-charge-limited current (SCLC) devices.

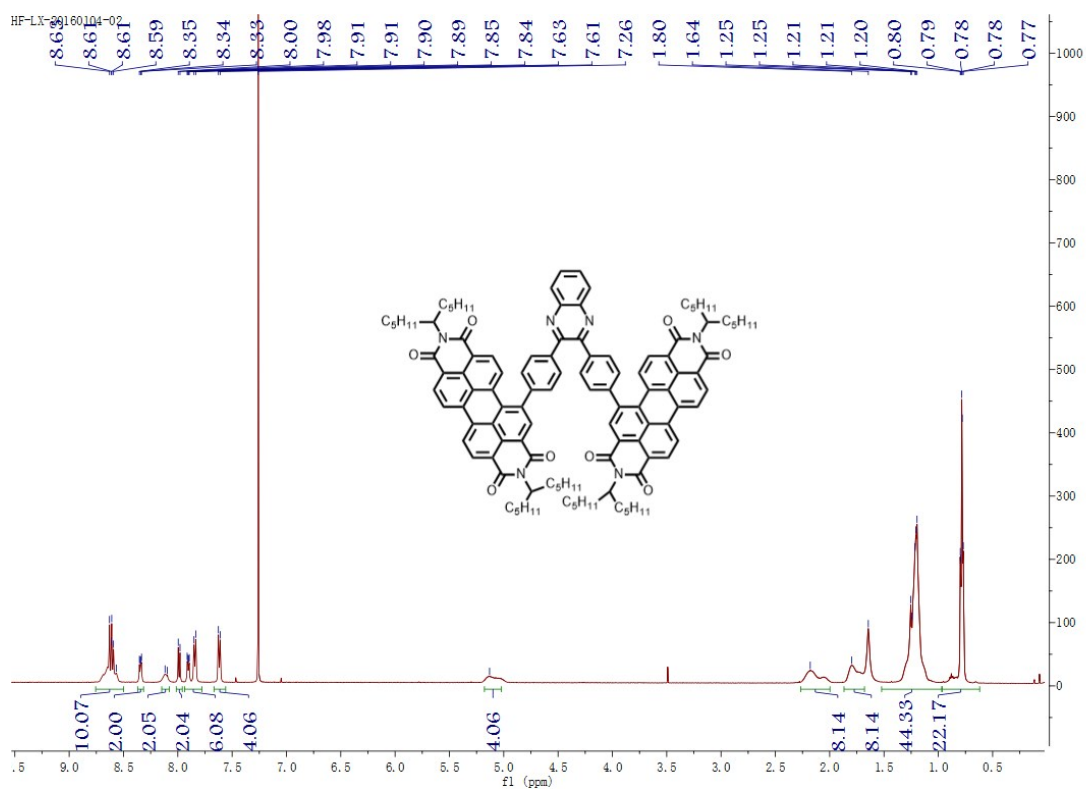
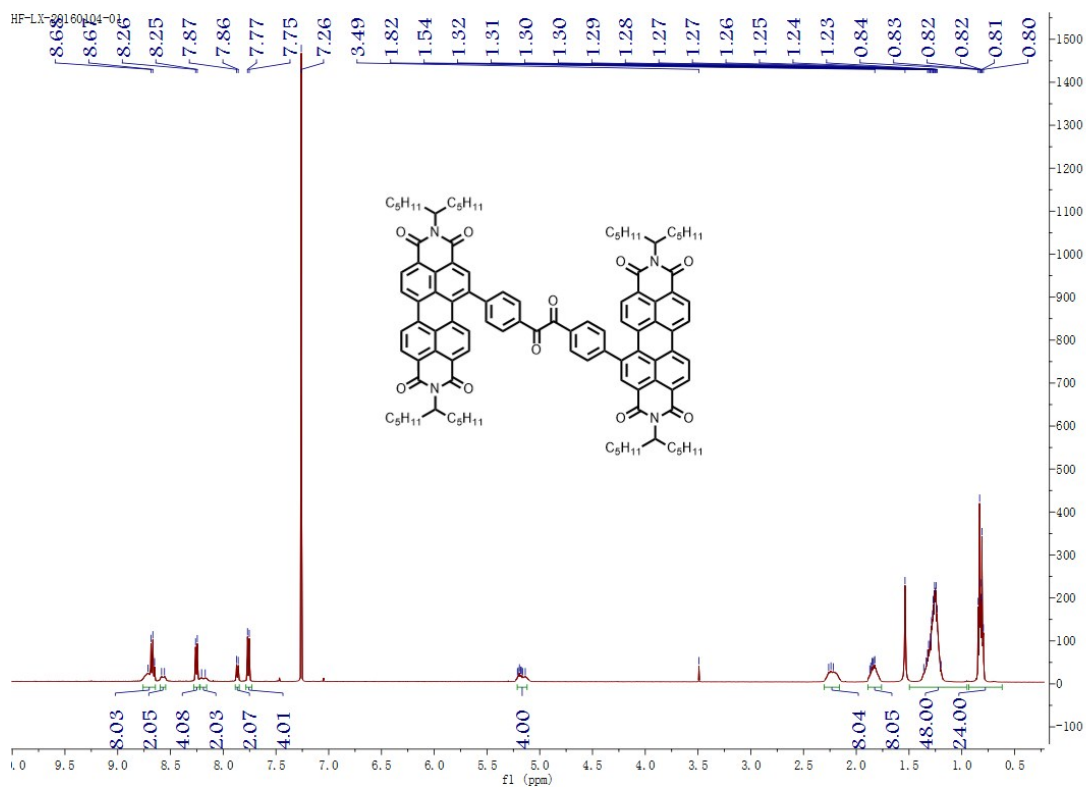
**Table S1** Photovoltaic properties of OSCs based on PDBT-T1 and the PDI acceptors under AM 1.5 G at 100 mW cm<sup>-2</sup>. The average values and standard deviation of device statistics from 10 devices.

PDBT-T1:PDIs	DIO (v/v)	$V_{oc}$ (V)	$J_{sc}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
P2O2	0%	0.910 ± 0.004	6.83 ± 0.10	34.8 ± 0.7	2.15 ± 0.08
	0.5%	0.876 ± 0.005	6.90 ± 0.08	41.4 ± 0.4	2.50 ± 0.04
P2N2	0%	0.963 ± 0.005	7.07 ± 0.14	37.6 ± 0.6	2.56 ± 0.08
	0.5%	0.946 ± 0.004	7.82 ± 0.10	50.8 ± 0.3	3.76 ± 0.08
P4N4	0%	0.982 ± 0.005	8.54 ± 0.12	49.7 ± 0.5	4.17 ± 0.08
	0.5%	0.957 ± 0.003	9.36 ± 0.07	62.6 ± 0.6	5.60 ± 0.09

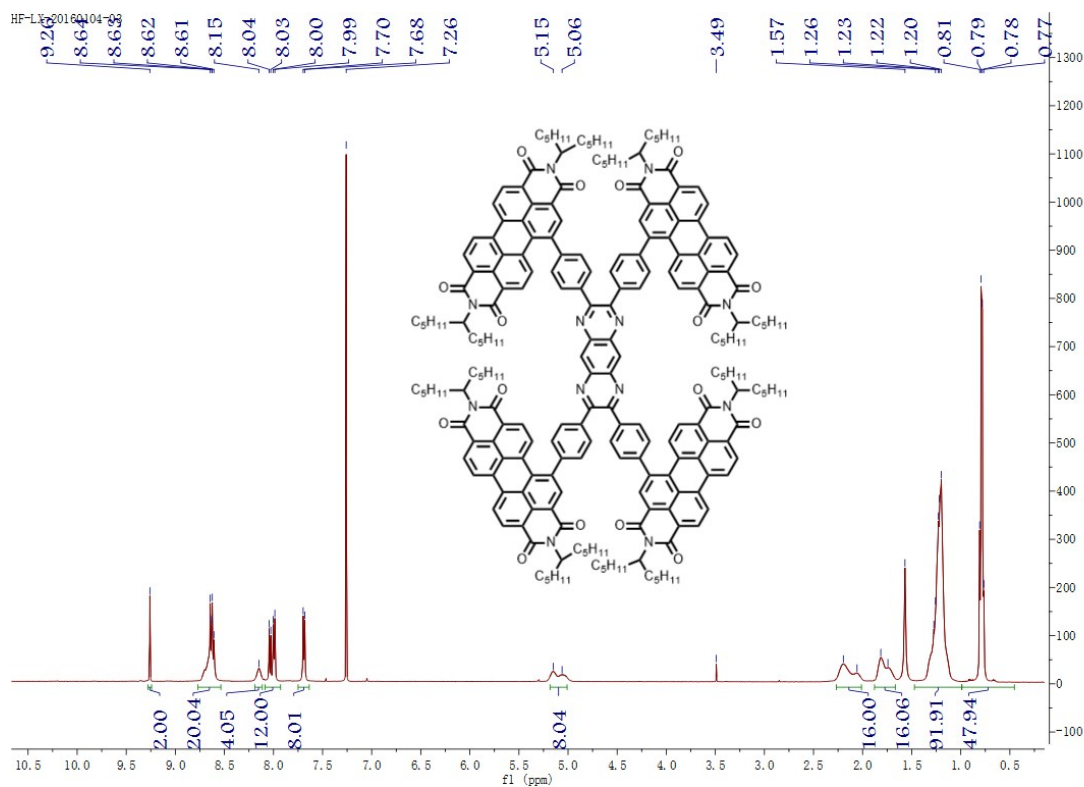
**Table S2** Photovoltaic properties of OSCs based on PTB7-Th and P4N4 under AM 1.5 G at 100 mW cm<sup>-2</sup>. The average values and standard deviation of device statistics from 10 devices.

	$V_{oc}$ (V)	$J_{sc}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%)	Best PCE (%)
(a)	0.78 ± 0.01	9.48 ± 0.15	32.94 ± 1.08	2.43 ± 0.09	2.58
(b)	0.84 ± 0.01	10.71 ± 0.10	41.05 ± 0.53	3.67 ± 0.06	3.72

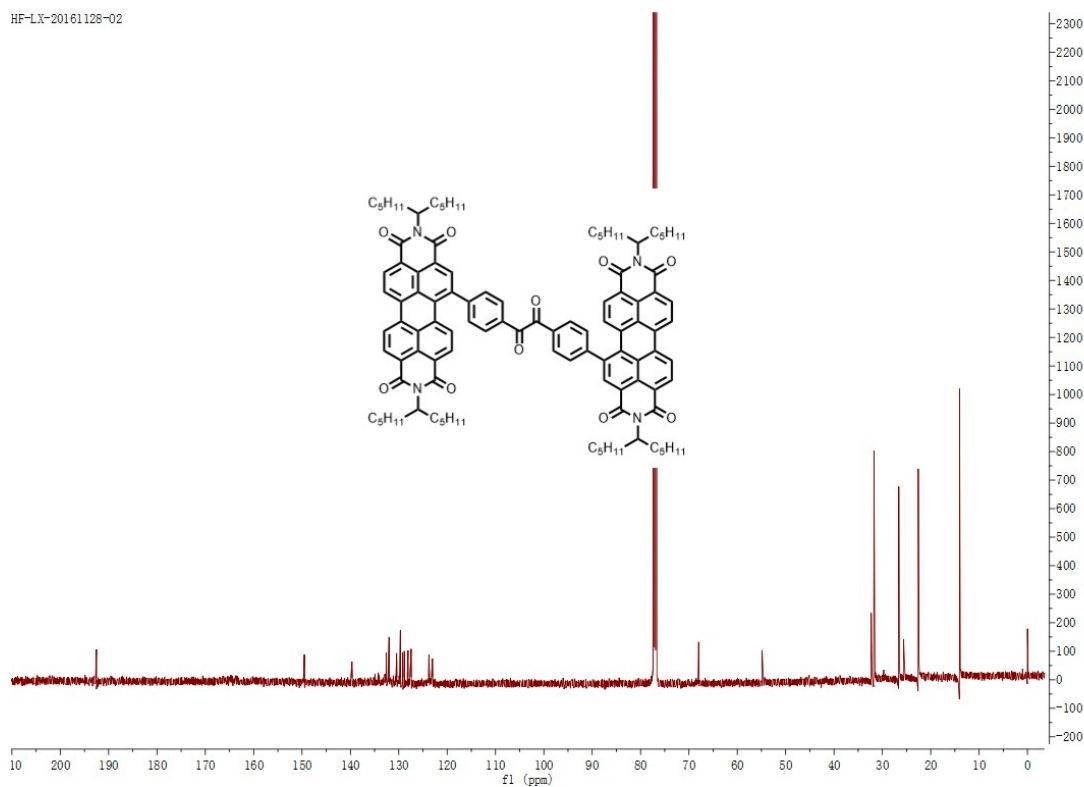
(a) device structure: ITO/PEDOT:PSS/PTB7-Th:P4N4/Ca/Al; (b) device structure: ITO/ZnO/PFN-OX/PTB7-Th:P4N4/MoO<sub>3</sub>/Ag.



**Fig. S6**  $^1\text{H}$  NMR spectrum of P2N2 solution in  $\text{CDCl}_3$ .

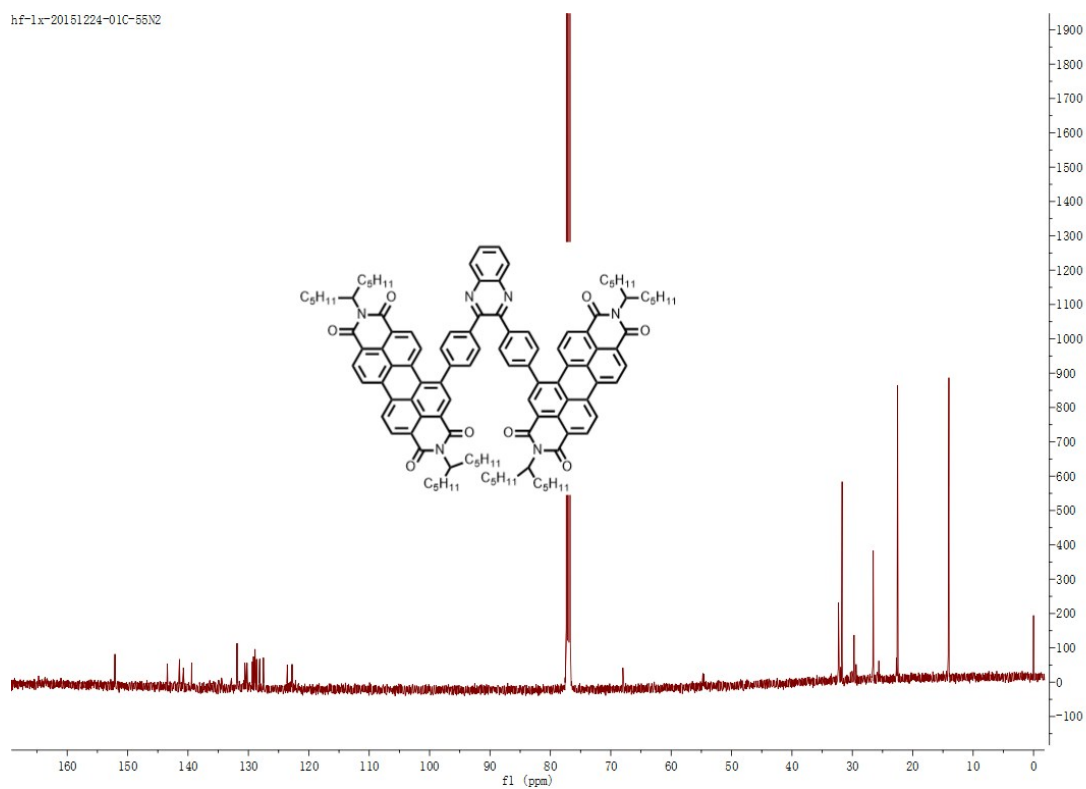


**Fig. S7**  $^1\text{H}$  NMR spectrum of P4N4 solution in  $\text{CDCl}_3$ .



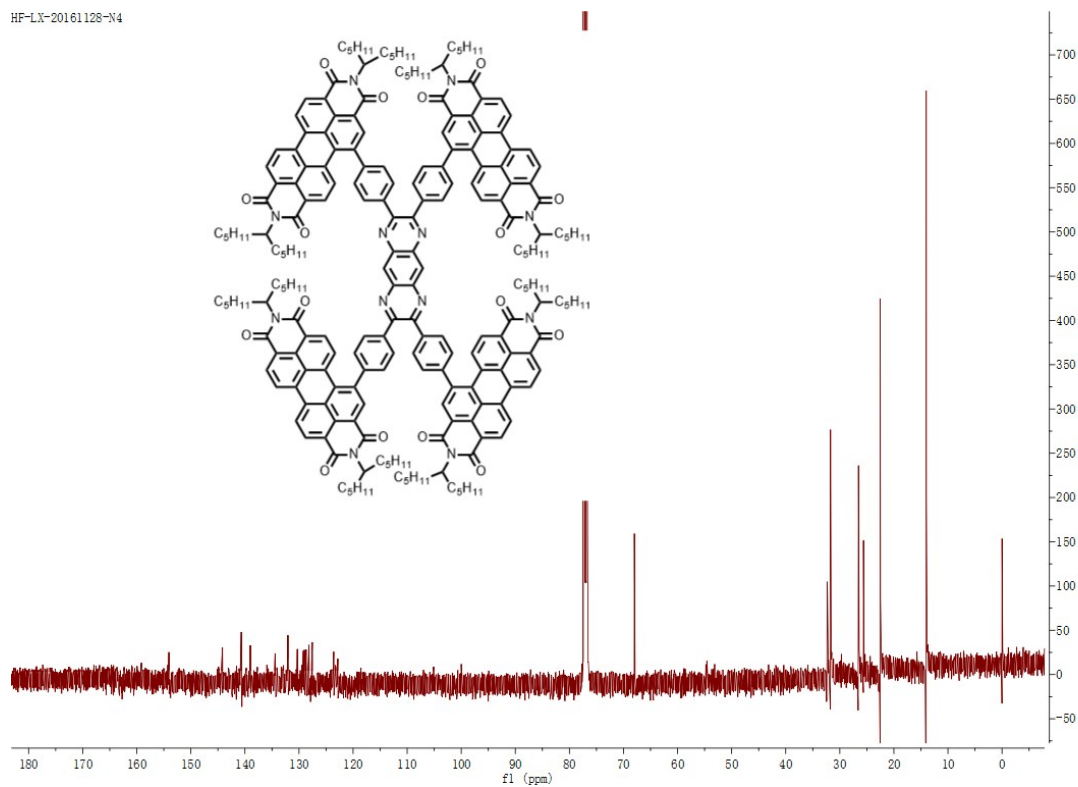
**Fig. S8**  $^{13}\text{C}$  NMR spectrum of P2O2 solution in  $\text{CDCl}_3$ .

hF-1x-20151224-01C-55N2

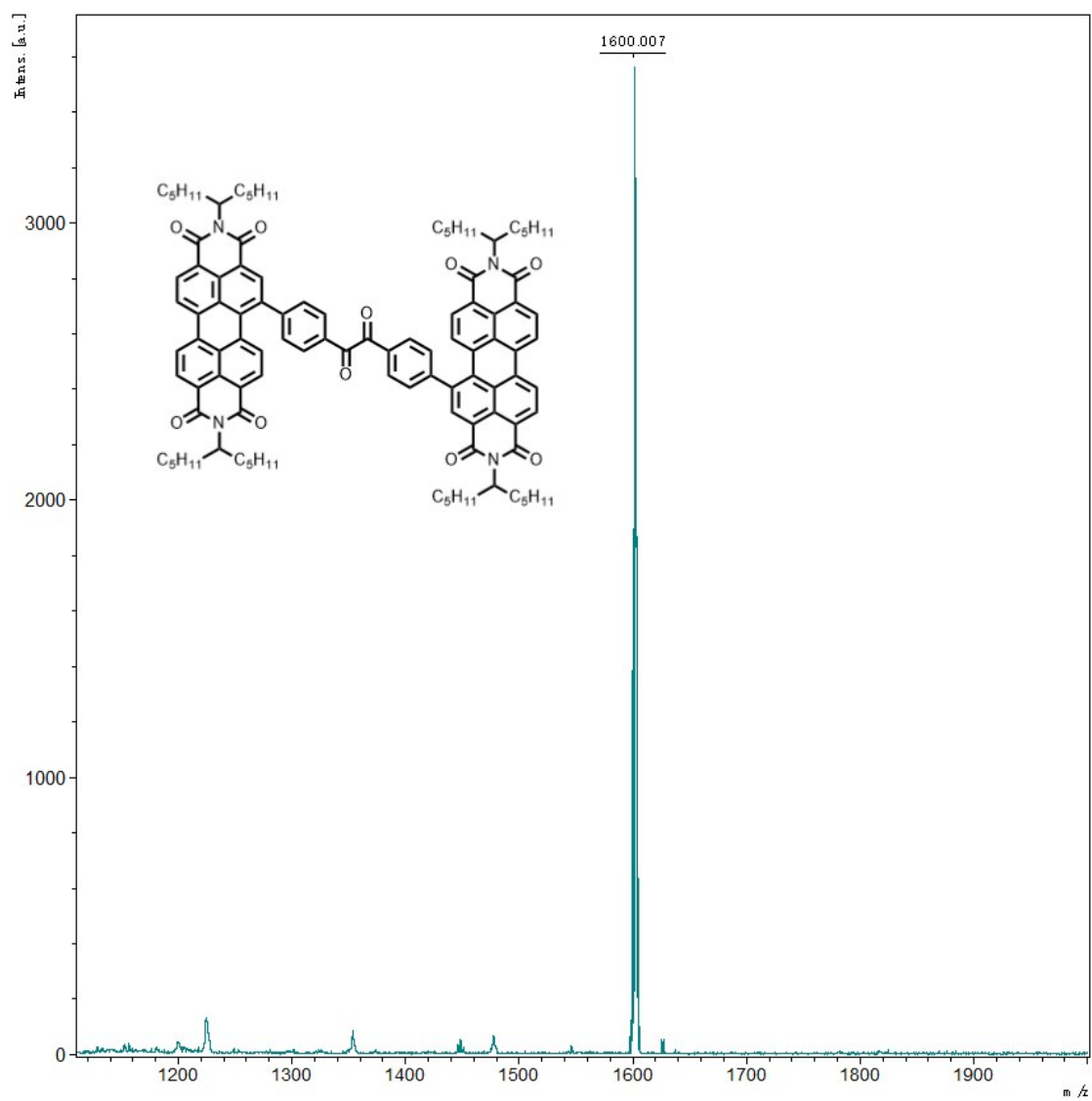


**Fig. S9** <sup>13</sup>C NMR spectrum of P2N2 solution in CDCl<sub>3</sub>.

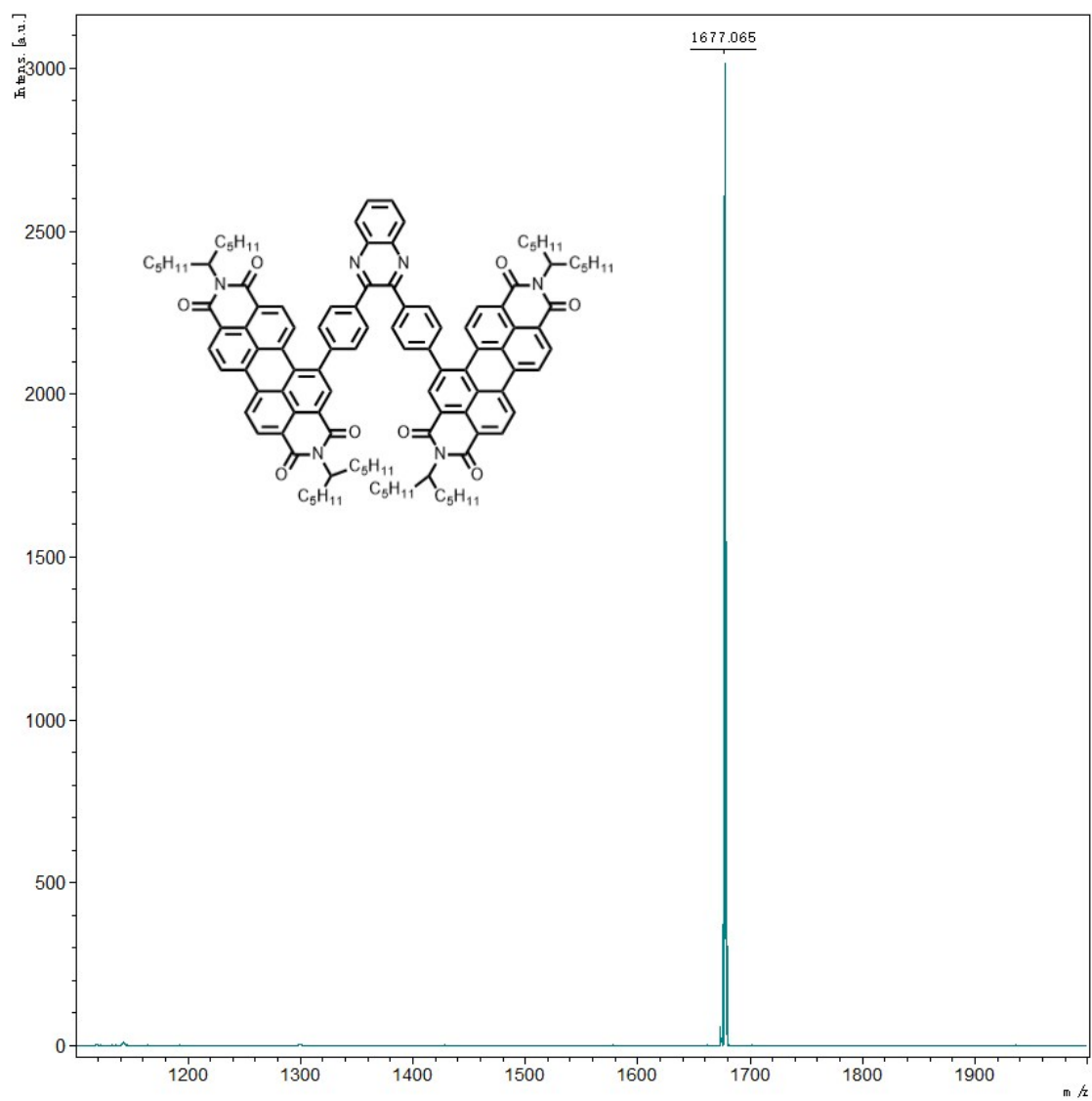
HF-LX-20161128-N4



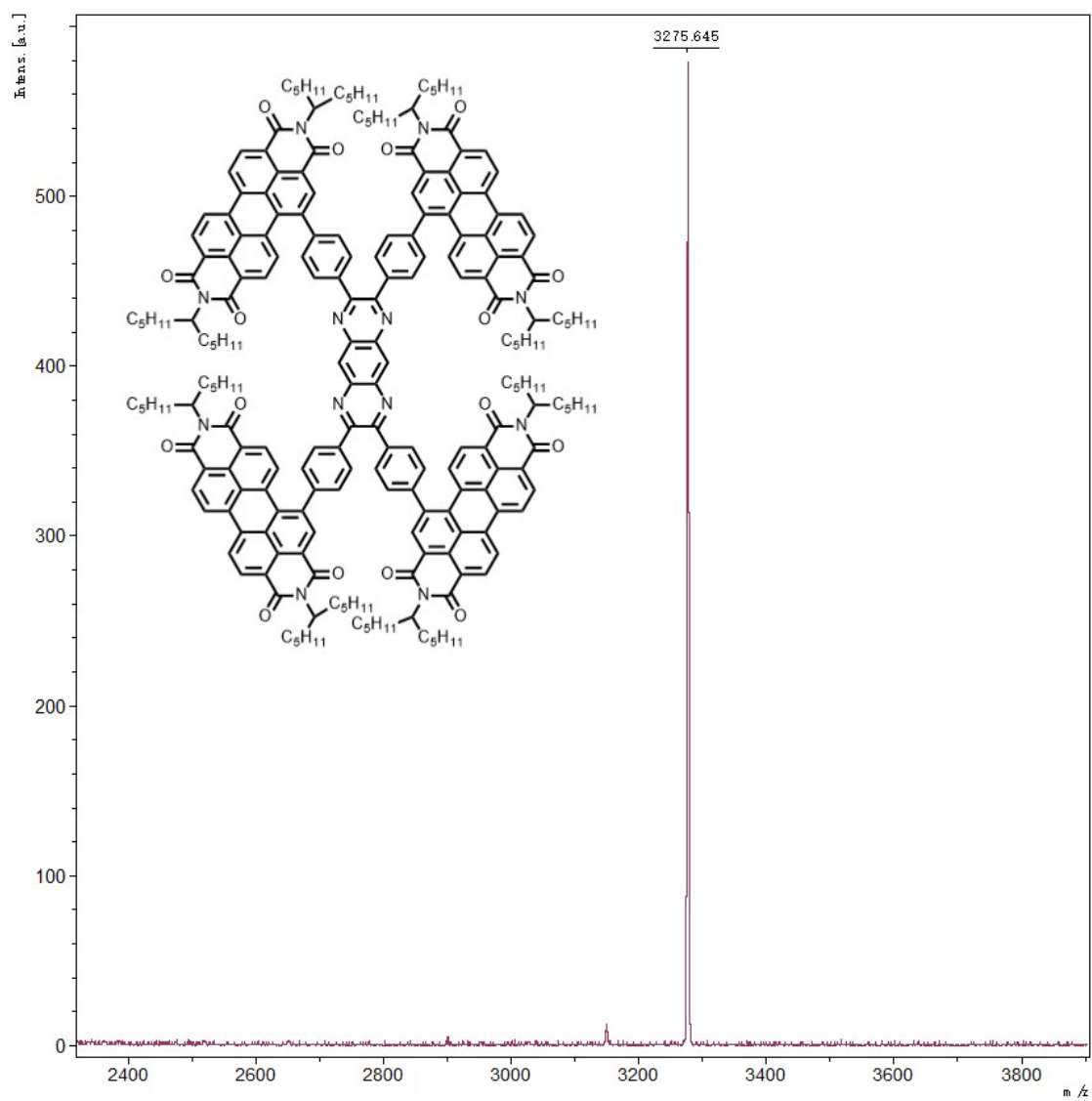
**Fig. S10** <sup>13</sup>C NMR spectrum of P4N4 solution in CDCl<sub>3</sub>.



**Fig. S11** Mass (MALDI-TOF) spectrum of P2O2.



**Fig. S12** Mass (MALDI-TOF) spectrum of P2N2.



**Fig. S13** Mass (MALDI-TOF) spectrum of P4N4.