Supporting Information for

Bis(perylene diimide) with DACH bridge as non-fullerene electron acceptor for organic solar cells

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Theoretical calculations

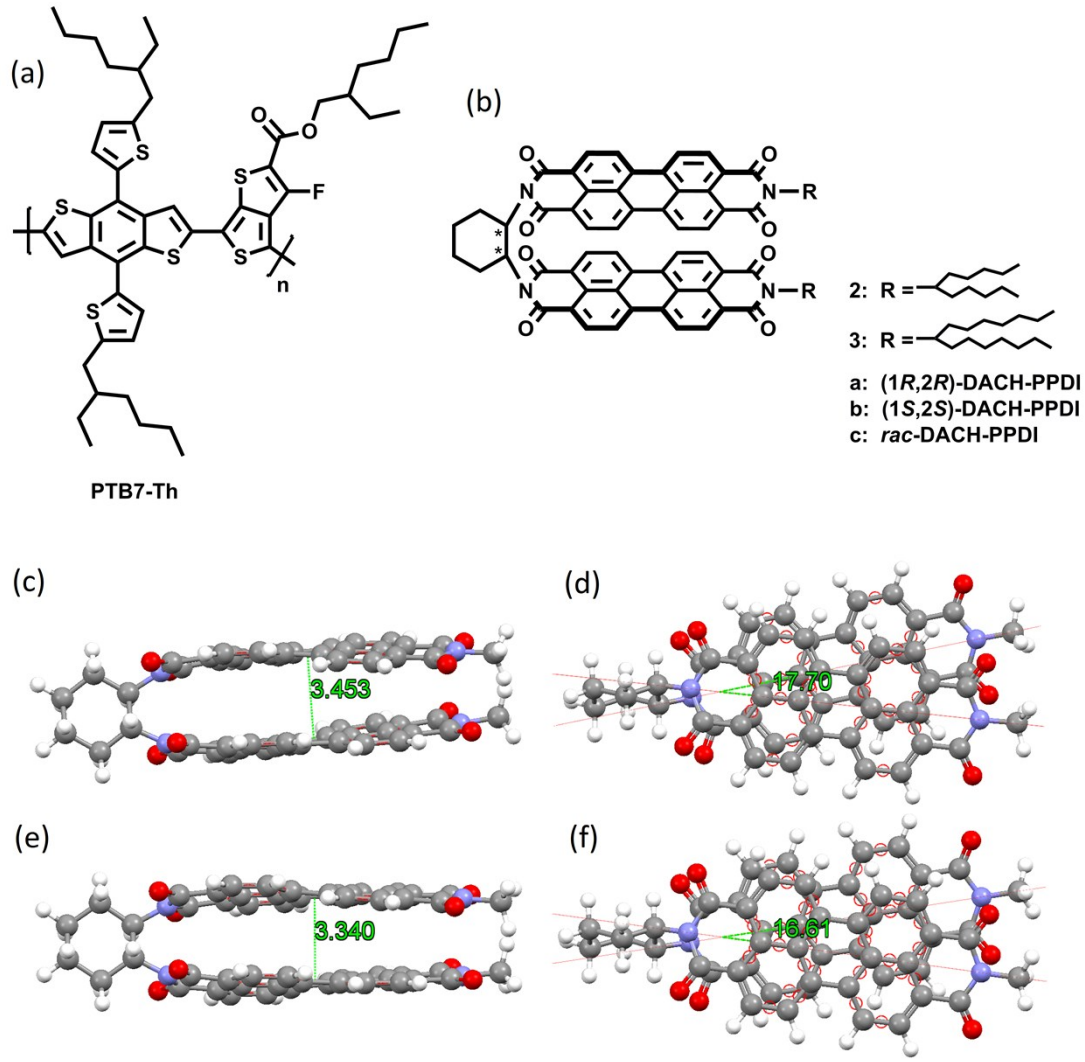
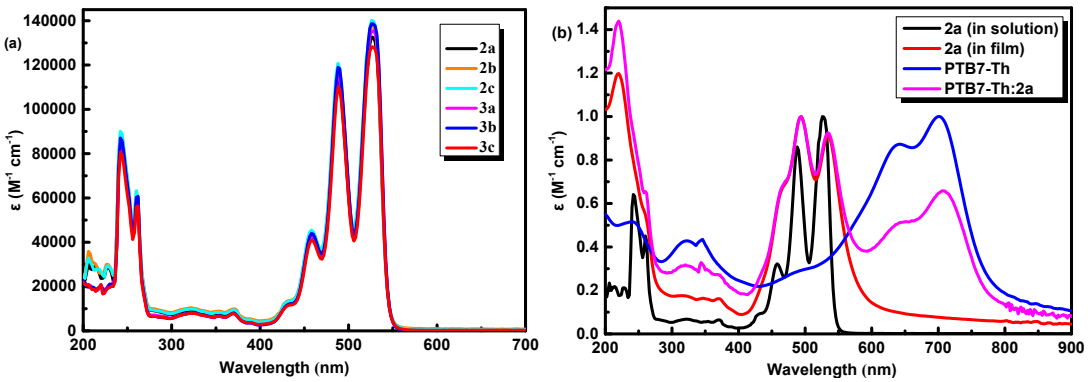


Figure S1. Chemical structures of PTB7-Th (a) and DACH-PPDIs (b). Optimized geometries of DACH-PPDI by DFT at the ωB97XD/6-31G(d) level (c, d) and APFD/6-31G(d) level (e, f).[1]

Optical, electrochemical and thermal Properties of DACH-PPDIs



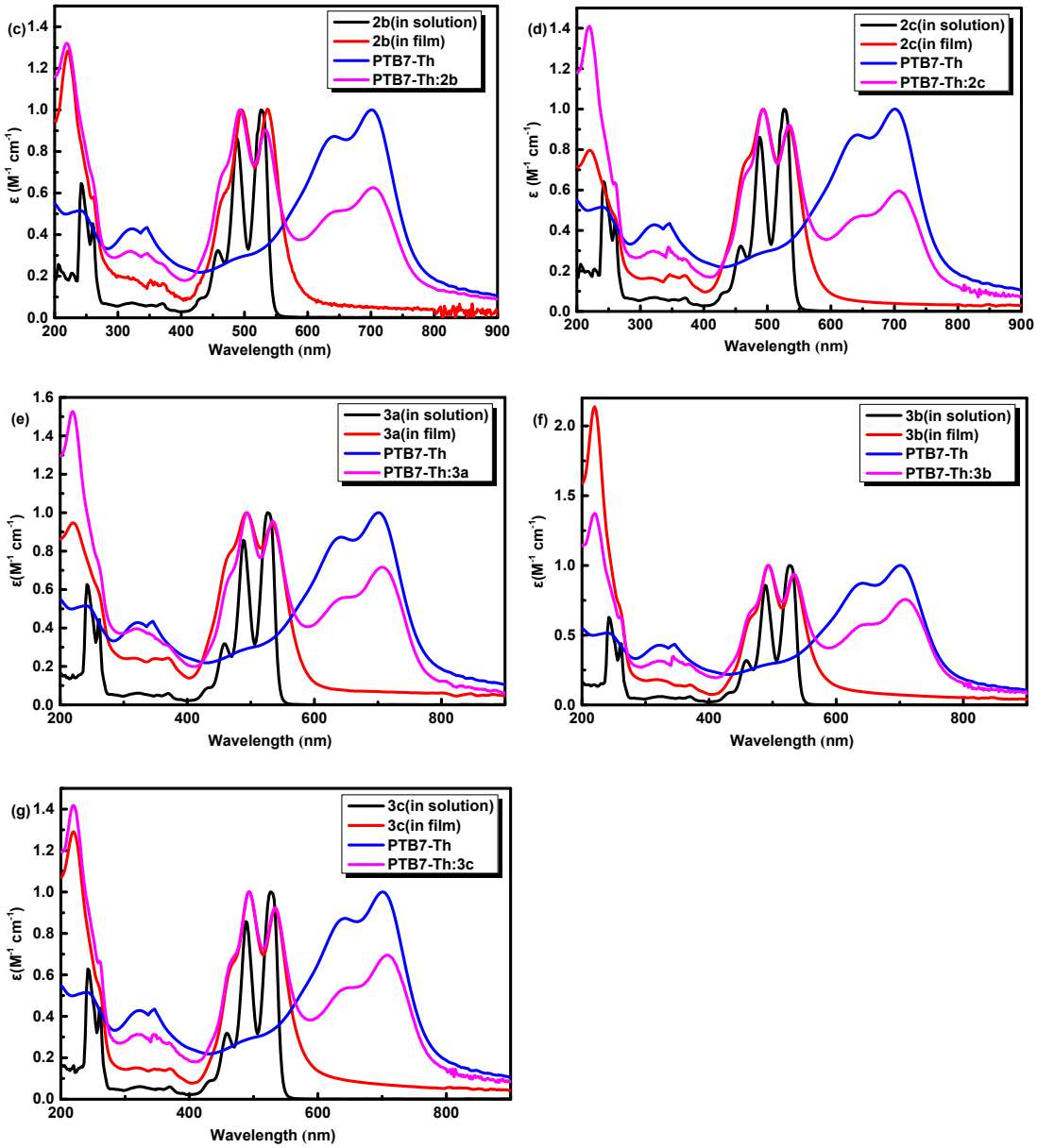


Figure S2. a) UV-Vis absorption spectra of **2** and **3** in chloroform solution (10^{-5} M). Normalized UV-Vis absorption spectra of b) **2a** in solution, **2a** and PTB7-Th in film on quartz substrate, PTB7-Th:**2a** blend film. c) **2b** in solution, **2b** and PTB7-Th in film on quartz substrate, PTB7-Th:**2b** blend film. d) **2c** in solution, **2c** and PTB7-Th in film on quartz substrate, PTB7-Th:**2c** blend film. e) **3a** in solution, **3a** and PTB7-Th in film on quartz substrate, PTB7-Th:**3a** blend film. f) **3b** in solution, **3b** and PTB7-Th in film on quartz substrate, PTB7-Th:**3b** blend film. g) **3c** in solution, **3c** and PTB7-Th in film on quartz substrate, PTB7-Th:**3c** blend film.

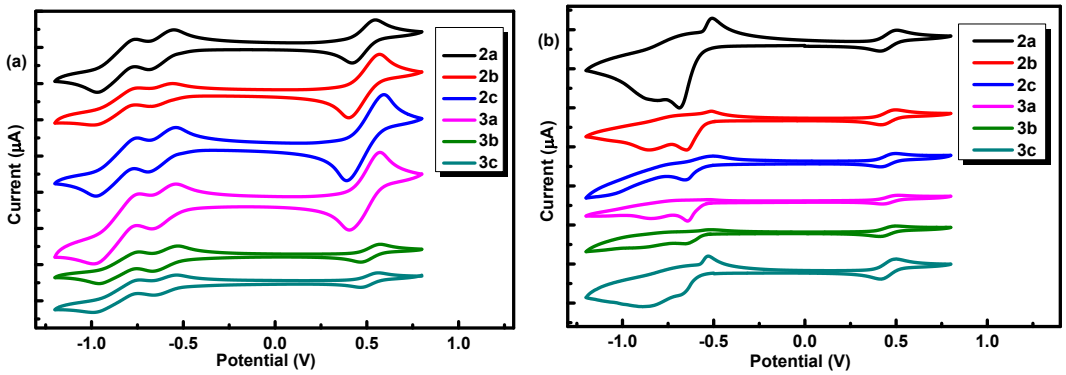


Figure S3. CVs of DACH-PPDIs in solution (a) and film (b). CVs were calibrated by the Fc/Fc^{+} as the redox couple and oxidation were from the reference compound ferrocene.

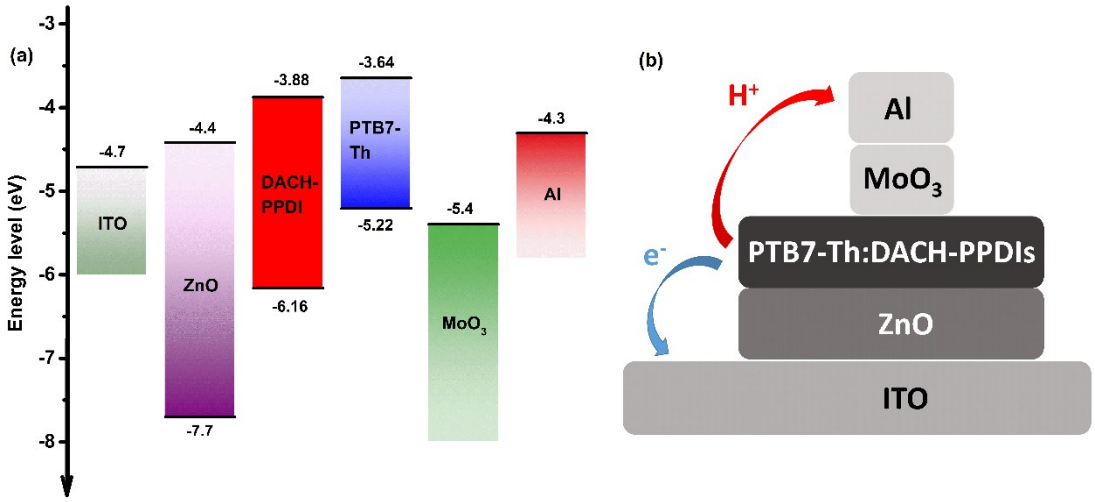


Figure S4 a) Energy levels of ITO, ZnO, DACH-PPDIs, PTB7-Th, MoO_3, and Al. b) The device architecture of non-fullerene OSCs.

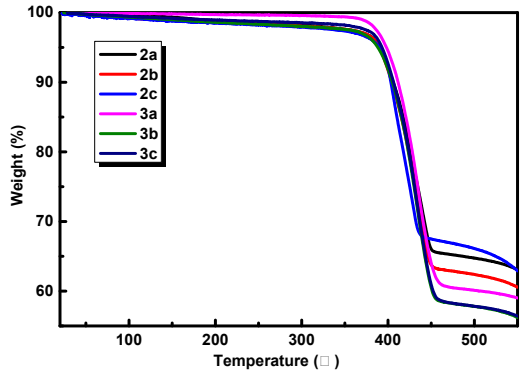


Figure S5. TGAs of DACH-PPDIs under nitrogen flow.

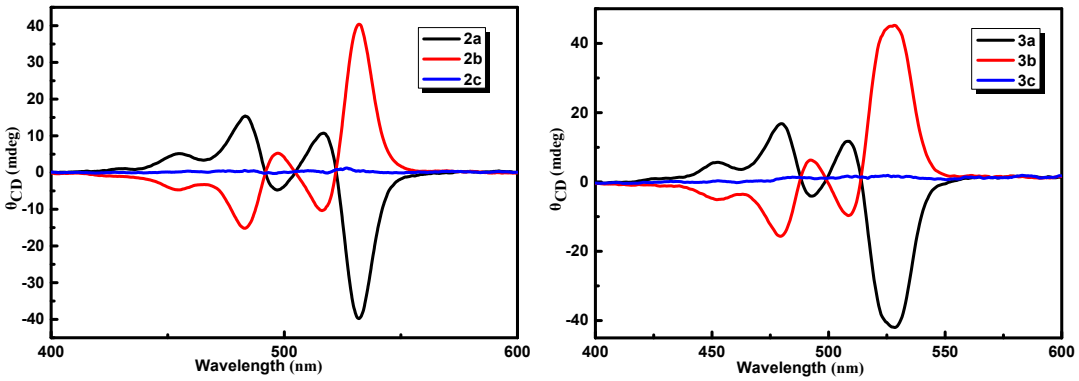


Figure S6. CD spectra of DACH-PPDIs in chloroform solution (10^{-5} M)

Photovoltaic performances

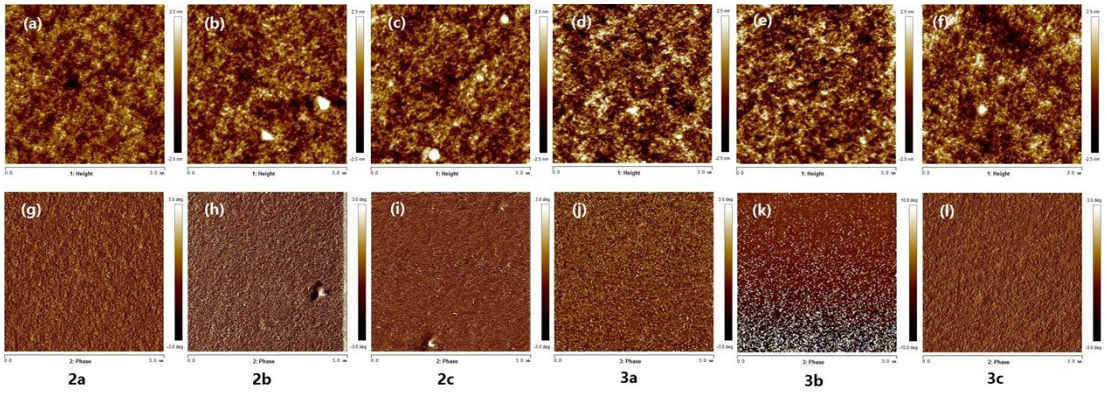
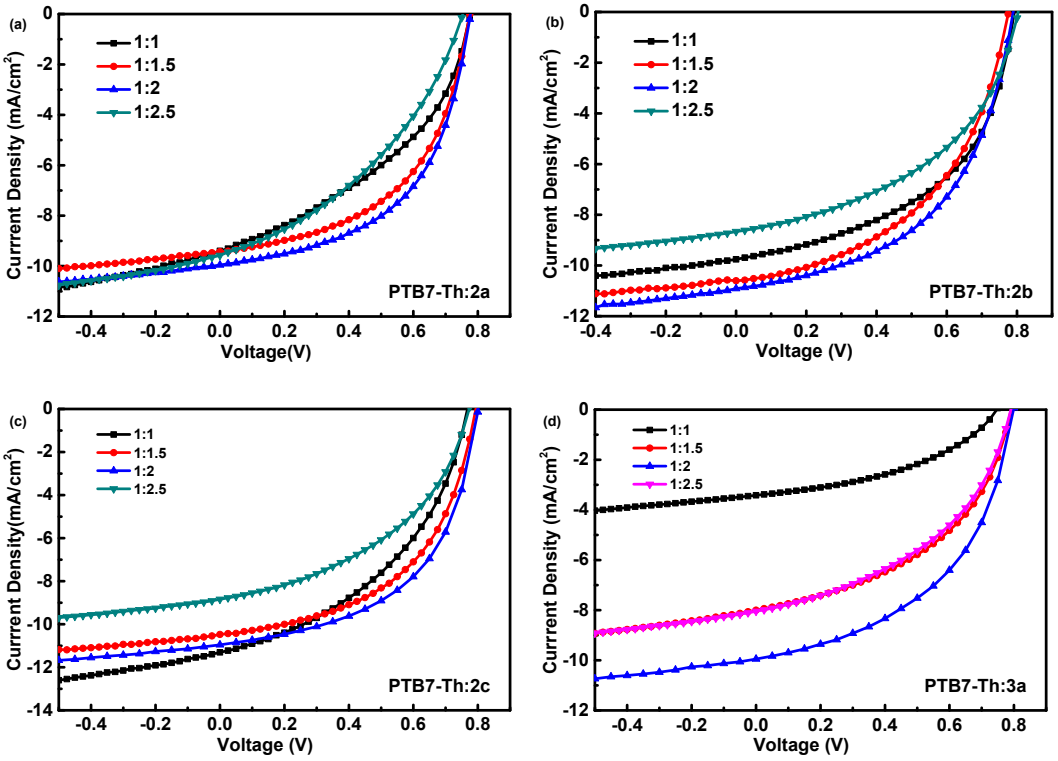


Figure S7. Tapping mode AFM height images (top) and phase images (bottom) of the active layers based on PTB7-Th:DACH-PPDIs, all images are 3 μm × 3 μm



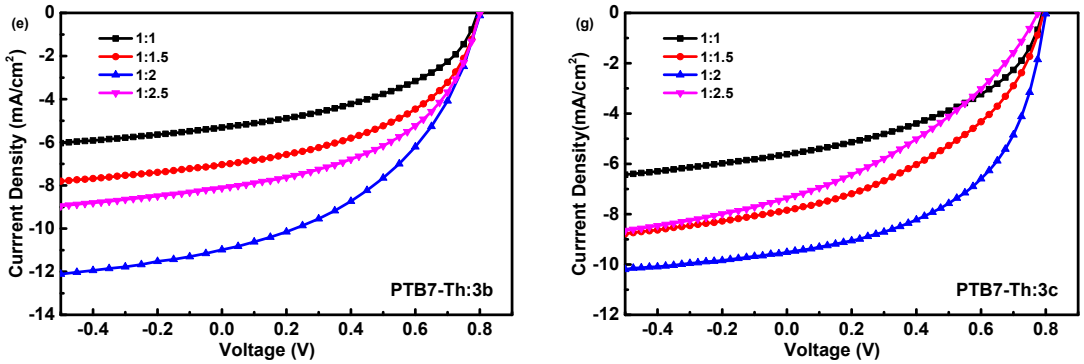


Figure S8. *J-V* curves of non-fullerene OSCs based on PTB7-Th with **2** and **3** by different ratio

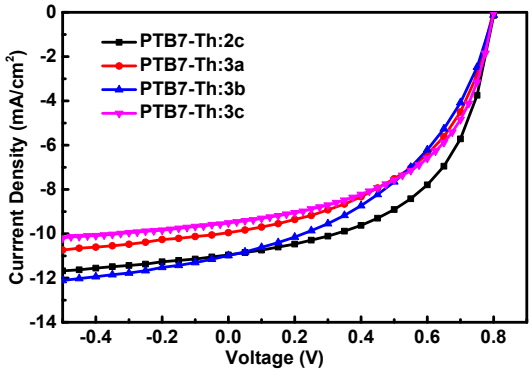


Figure S9. *J-V* curves of non-fullerene OSCs based on PTB7-Th with **2c** and **3a-3c**, respectively. (1:2 ratio, w:w)

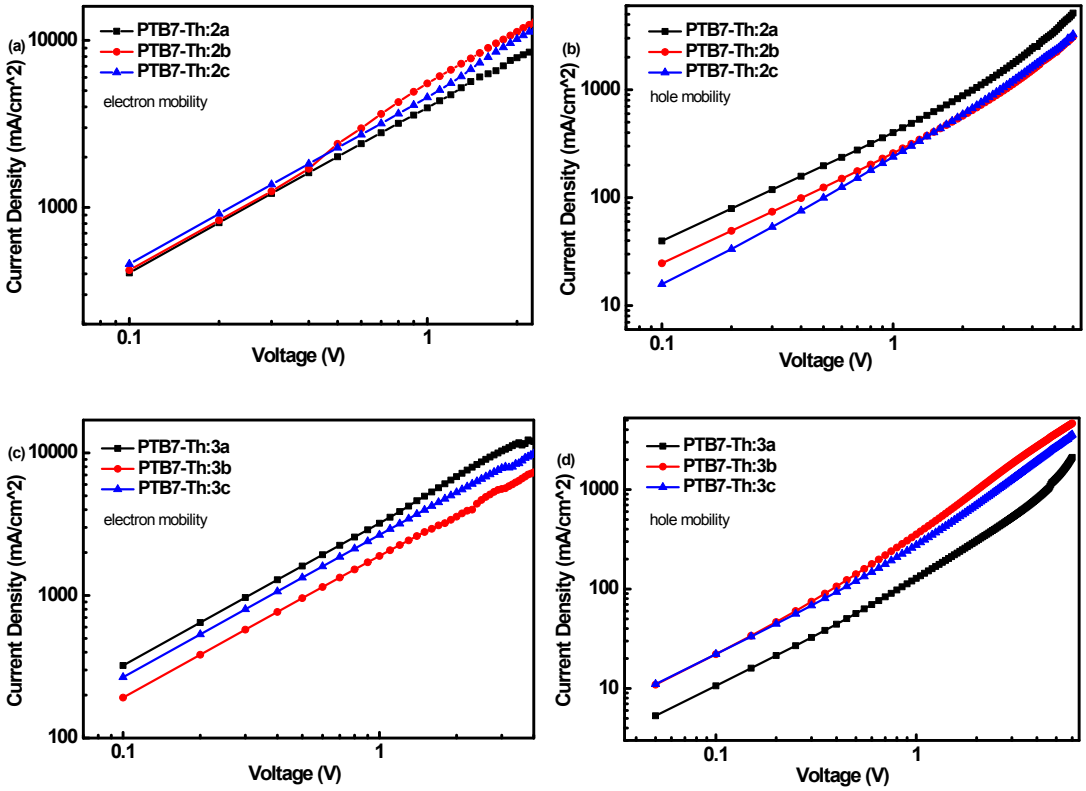


Figure 10. Measured space-charge-limited *J–V* characteristics of PTB7-Th:DACH-PPDIs blend films under dark conditions for electron-only devices and hole-only devices

Table S1. Photophysical, electrochemical and thermal properties of DACH-PPDIs

	$\lambda_{max}^{sol.}$ [nm] [a]	ε [$M^{-1}cm^{-1}$] [a]	λ_{max}^{film} [nm] [b]	E_g [eV] [c]	E_{onset}^{re} [V] [d]	E_{LUMO} [eV] [e]	E_{HOMO} [eV] [f]	T_{deg} [ºC] [g]
2a	**526**	**132703**	**494**	**2.28**	**-0.92**	**-3.88**	**-6.16**	**397**
2b	**526**	**137768**	**496**	**2.28**	**-0.92**	**-3.88**	**-6.16**	**398**
2c	**526**	**140160**	**494**	**2.28**	**-0.92**	**-3.88**	**-6.16**	**392**
3a	**526**	**135399**	**494**	**2.27**	**-0.92**	**-3.88**	**-6.15**	**401**
3b	**526**	**138677**	**494**	**2.27**	**-0.92**	**-3.88**	**-6.15**	**403**
3c	**526**	**128232**	**492**	**2.27**	**-0.92**	**-3.88**	**-6.15**	**401**

[a] Measured in dilute $CHCl_3$ solution (1.0×10^{-5} M). [b] Measured in spin-coating film from $CHCl_3$ solution. [c] Calculated by the onset of absorption in $CHCl_3$ solution according to E_g (eV) = ($1240/\lambda_{onset}$). [d] In CH_2Cl_2 solution vs. Fc/Fc^+. [e] LUMO (eV) estimated by the onset of the reduction peaks and calculated according to E_{LUMO} = -(4.8 + E_{onset}^{re}) eV. [f] HOMO (eV) calculated according to E_{HOMO} = (E_{LUMO} - E_g) eV. [g] Decomposition temperature determined by TGA corresponding to 5% weight loss at 10 ºC/min under nitrogen flow.

Table S2. The performances of PTB7-Th:**2c** blend based devices (1:2, w/w) under different annealing temperature

D/A ratio	Annealing temperature (ºC)	V_{oc} (V)	J_{sc} (mA cm^{-2})	*FF* (%)	*PCE* (%)[a]
1:2	**--**	**0.79 ± 0.007**	**7.19 ± 0.19**	**51.80 ± 1.67**	**2.95 ± 0.05 (3.00)**
1:2	**70**	**0.80 ± 0.006**	**10.63 ± 0.39**	**51.40 ± 1.56**	**4.34 ± 0.20 (4.68)**
1:2	**90**	**0.77 ± 0.014**	**9.81 ± 0.46**	**45.15 ± 0.94**	**3.40 ± 0.10 (3.48)**

[a] Tested under the illumination of AM 1.5 G 100 mW/cm^2. The values in parentheses refer to the max PCEs obtained from over five devices.

Table S3. The detailed photovoltaic values of the non-fullerene devices with an inverted structure based on PTB7-Th:DACH-PPDIs **2** and **3** by different ratios (w/w), under the annealing temperature of 70 ºC

D/A	D/A ratio	V_{oc} (V)	J_{sc} (mA cm^{-2})	*FF* (%)	*PCE* (%)[a]
PTB7-Th/2a	**1:1**	**0.76 ± 0.017**	**9.73 ± 0.24**	**41.12 ± 1.47**	**3.05 ± 0.11 (3.25)**
	1:1.5	**0.78 ± 0.014**	**9.63 ± 0.36**	**49.48 ± 1.65**	**3.70 ± 0.10 (3.81)**
	1:2	**0.77 ± 0.006**	**10.52 ± 0.37**	**50.40 ± 1.63**	**4.09 ± 0.15 (4.36)**

	1:2.5	0.77 ± 0.007	8.54 ± 0.43	44.28 ± 1.42	2.92 ± 0.11 (3.05)

D/A	D/A ratio	V_{oc} (V)	J_{sc} (mA cm^{-2})	*FF* (%)	*PCE* (%)
PTB7-Th/2b	1:1	0.78 ± 0.008	9.54 ± 0.34	49.20 ± 2.00	3.66 ± 0.14 (3.91)
	1:1.5	0.78 ± 0.012	9.64 ± 0.49	50.20 ± 1.25	3.79 ± 0.19 (4.01)
	1:2	0.79 ± 0.003	10.47 ± 0.34	51.47 ± 0.56	4.25 ± 0.11 (4.42)
	1:2.5	0.79 ± 0.008	8.30 ± 0.19	45.85 ± 1.26	3.00 ± 0.13 (3.24)

D/A	D/A ratio	V_{oc} (V)	J_{sc} (mA cm^{-2})	*FF* (%)	*PCE* (%)
PTB7-Th/2c	1:1	0.77 ± 0.012	10.92 ± 0.43	42.20 ± 1.30	3.54 ± 0.21 (3.81)
	1:1.5	0.79 ± 0.005	9.60 ± 0.51	52.00 ± 1.07	3.95 ± 0.19 (4.29)
	1:2	0.80 ± 0.006	10.63 ± 0.39	51.40 ± 1.56	4.34 ± 0.20 (4.68)
	1:2.5	0.77 ± 0.009	7.74 ± 0.30	35.26 ± 1.56	2.10 ± 0.16 (2.38)

D/A	D/A ratio	V_{oc} (V)	J_{sc} (mA cm^{-2})	*FF* (%)	*PCE* (%)
PTB7-Th/3a	1:1	0.67 ± 0.052	3.18 ± 0.38	41.60 ± 0.92	0.89 ± 0.17 (1.09)
	1:1.5	0.79 ± 0.002	7.27 ± 0.61	47.48 ± 1.92	2.73 ± 0.20 (2.95)
	1:2	0.79 ± 0.010	9.56 ± 0.33	50.03 ± 1.12	3.78 ± 0.05 (3.87)
	1:2.5	0.79 ± 0.004	7.82 ± 0.25	45.04 ± 1.49	2.79 ± 0.05 (2.84)

D/A	D/A ratio	V_{oc} (V)	J_{sc} (mA cm^{-2})	*FF* (%)	*PCE* (%)
PTB7-Th/3b	1:1	0.79 ± 0.005	5.04 ± 0.48	45.06 ± 1.59	1.79 ± 0.12 (1.92)
	1:1.5	0.80 ± 0.008	6.53 ± 0.68	46.20 ± 1.70	2.40 ± 0.23 (2.69)
	1:2	0.80 ± 0.006	9.51 ± 0.15	49.78 ± 1.15	3.80 ± 0.06 (3.85)
	1:2.5	0.80 ± 0.007	7.37 ± 0.45	51.44 ± 1.62	3.03 ± 0.09 (3.17)

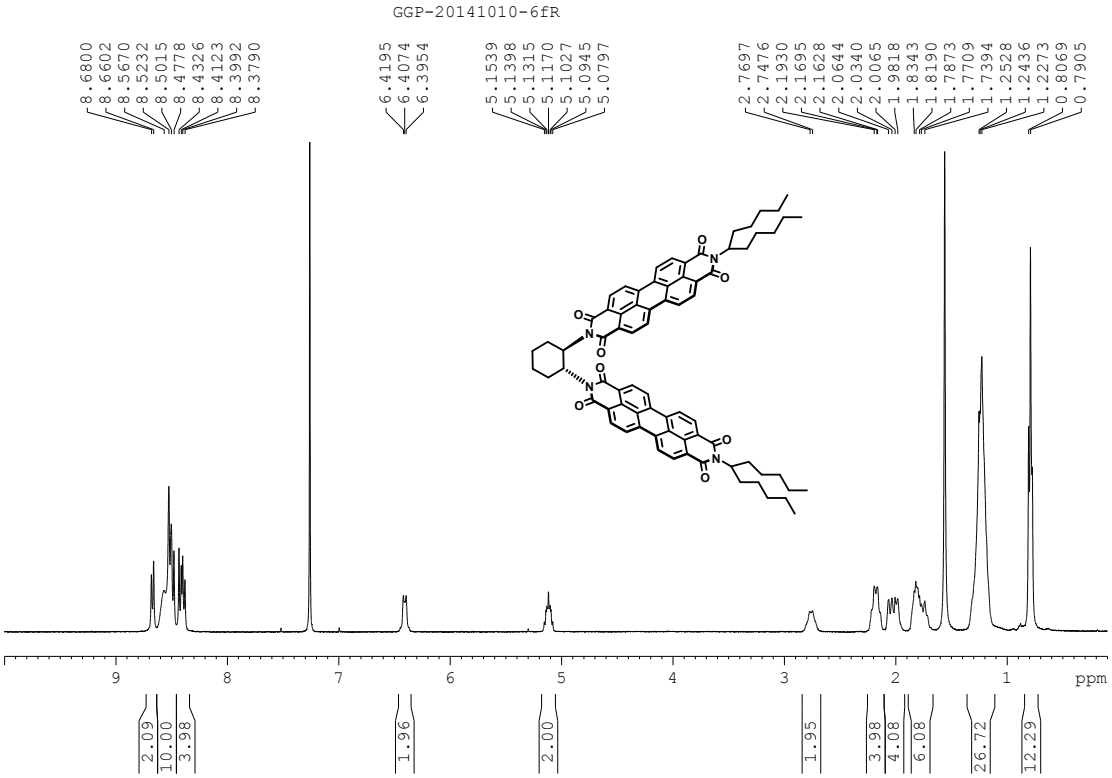
D/A	D/A ratio	V_{oc} (V)	J_{sc} (mA cm^{-2})	*FF* (%)	*PCE* (%)
PTB7-Th/3c	1:1	0.78 ± 0.009	5.35 ± 0.22	43.48 ± 1.78	1.81 ± 0.16 (1.97)
	1:1.5	0.79 ± 0.008	7.46 ± 0.31	44.06 ± 1.31	2.59 ± 0.06 (2.66)
	1:2	0.81 ± 0.007	9.55 ± 0.23	50.55 ± 1.47	3.90 ± 0.06 (3.97)
	1:2.5	0.79 ± 0.006	6.91 ± 0.55	34.55 ± 0.97	1.87 ± 0.16 (2.07)

[a] Tested under the illumination of AM 1.5 G 100 mW/cm^2. The values in parentheses refer to the max PCEs obtained from over five devices.

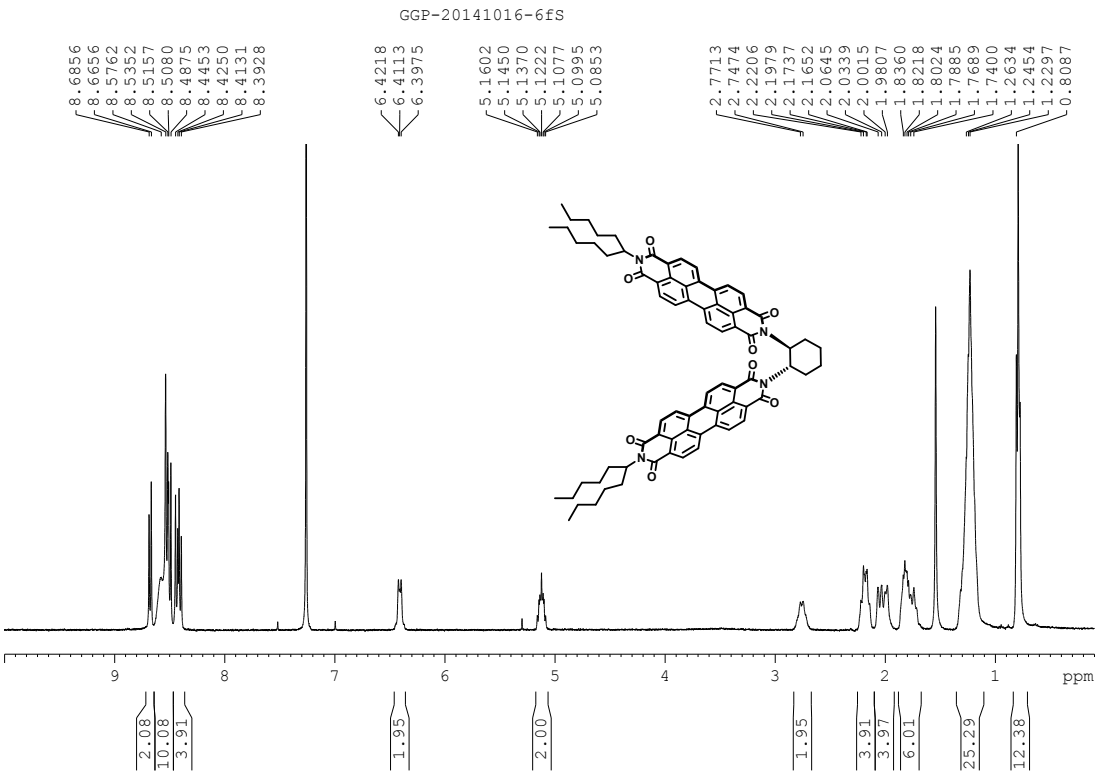
References:

1. (a) J. -D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.*,2008, **10**, 6615–6620; (b) A. Austin, G. A. Petersson, M. J. Frisch, F. J. Dobek, G. Scalmani, and K. Throssell, *J. Chem. Theory Comput*., 2012, **8**, 4989−5007; (c) M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees and J. A. Pople, *J. Chem. Phys.*, 1982, **77**, 3654-3665; (d) Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

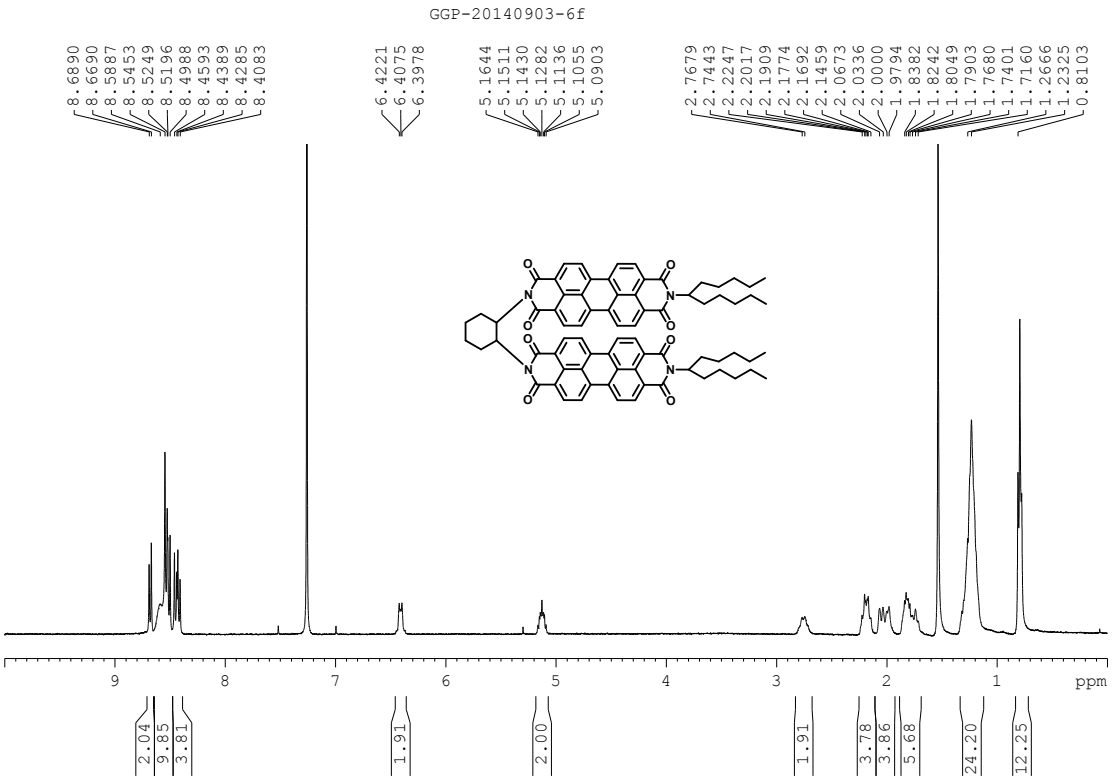
^{1}H NMR spectrum of **2a** in $CDCl_3$ (400 MHz, 25 ºC).



^{1}H NMR spectrum of **2b** in $CDCl_3$ (400 MHz, 25 ºC).



^{1}H NMR spectrum of **2c** in $CDCl_3$ (400 MHz, 25 ºC).



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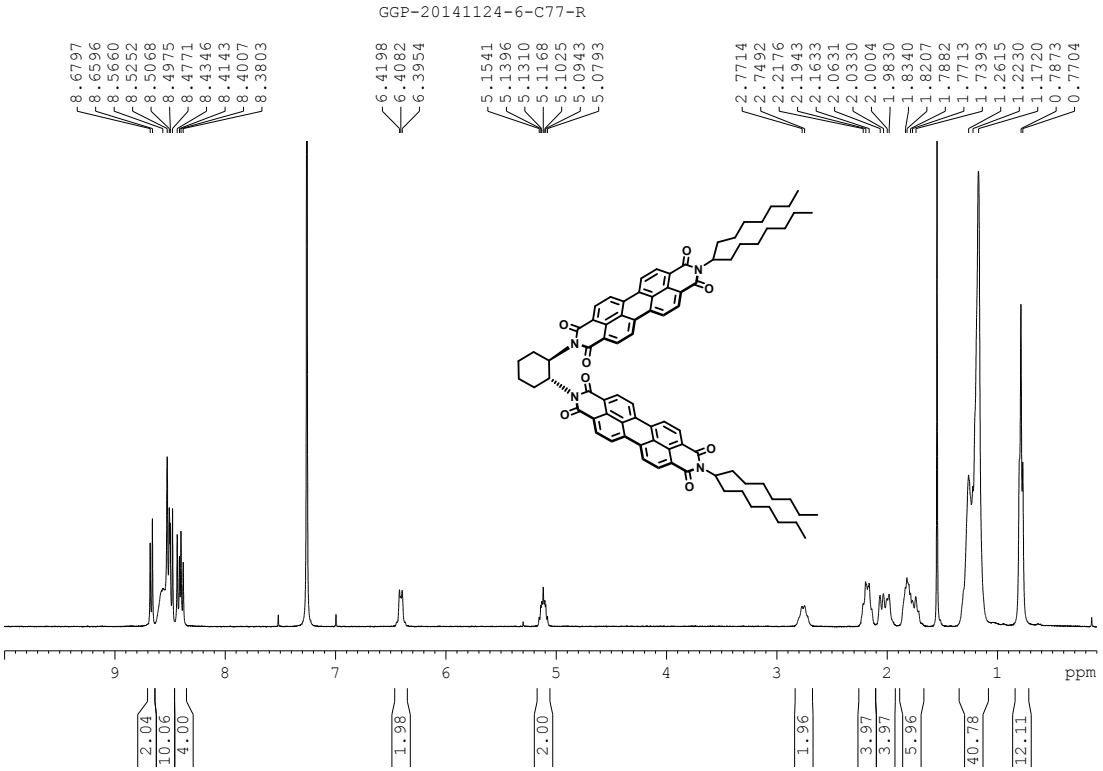

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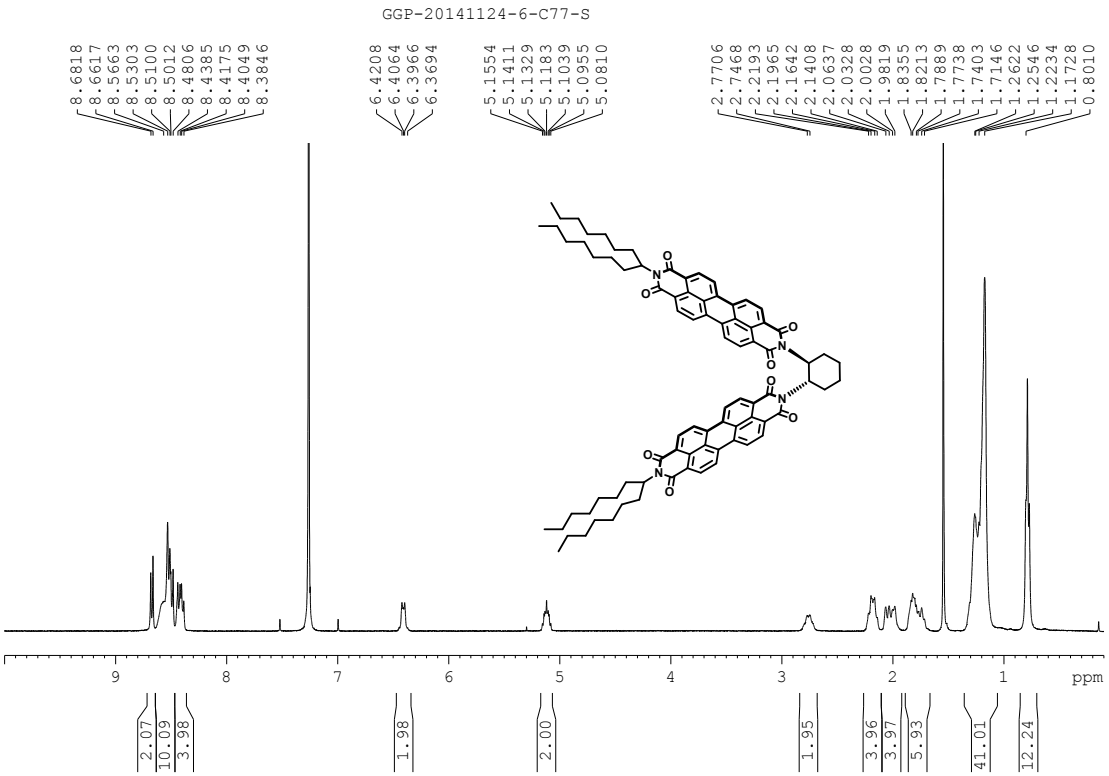

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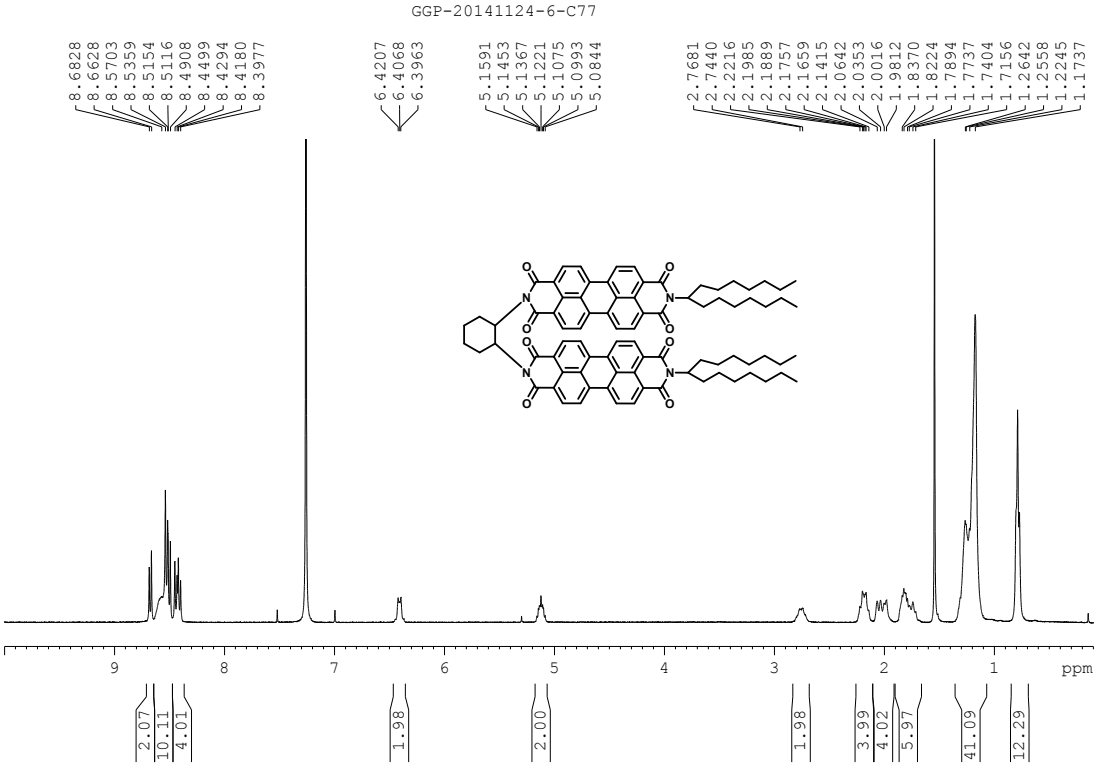
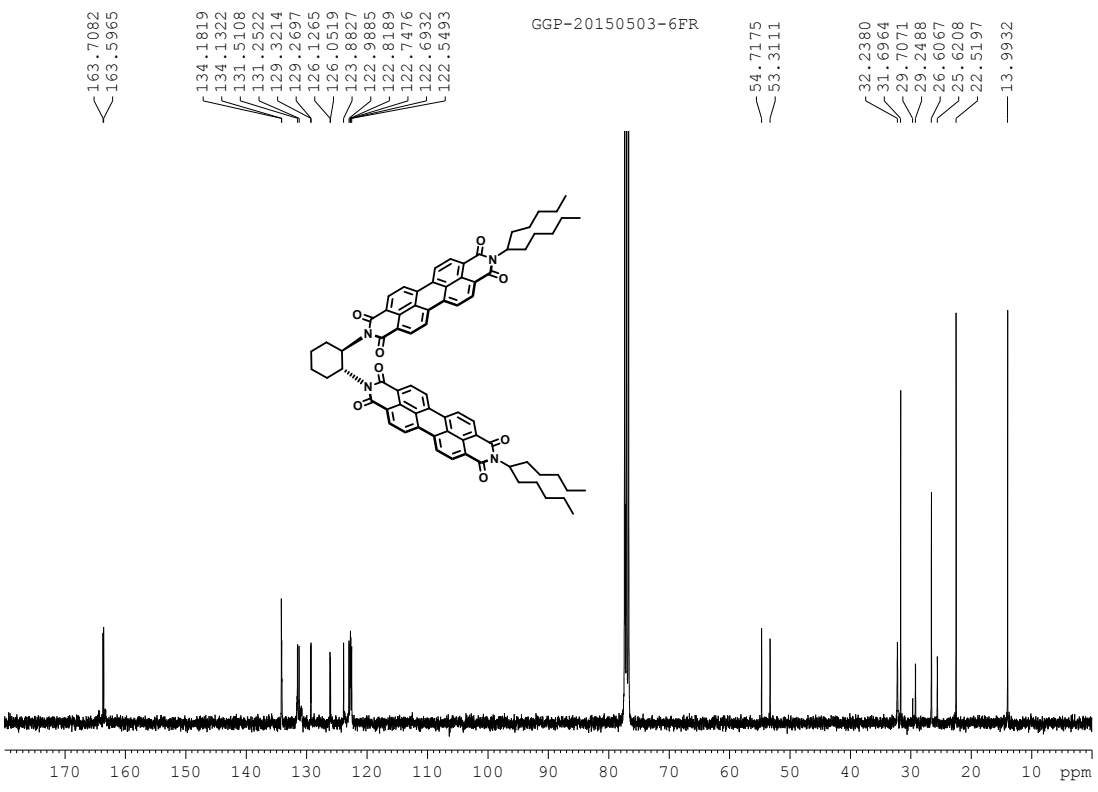


^{13}C NMR spectrum of **2a** in $CDCl_3$ (100 MHz, 25 ºC).



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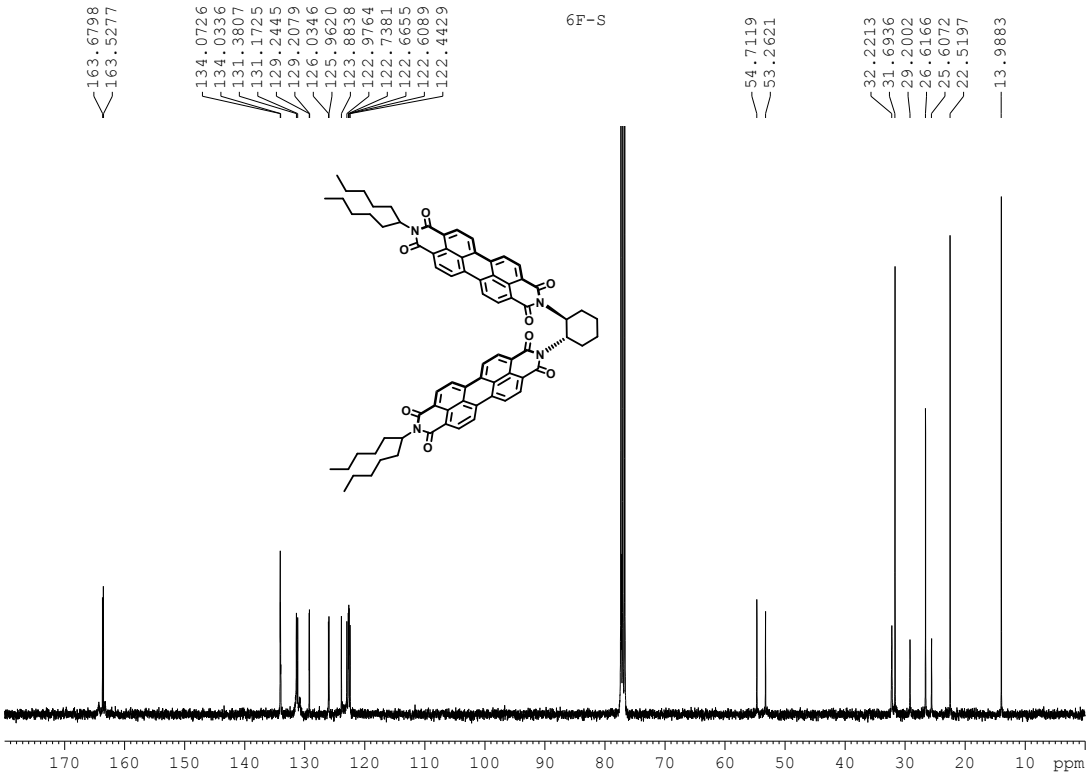

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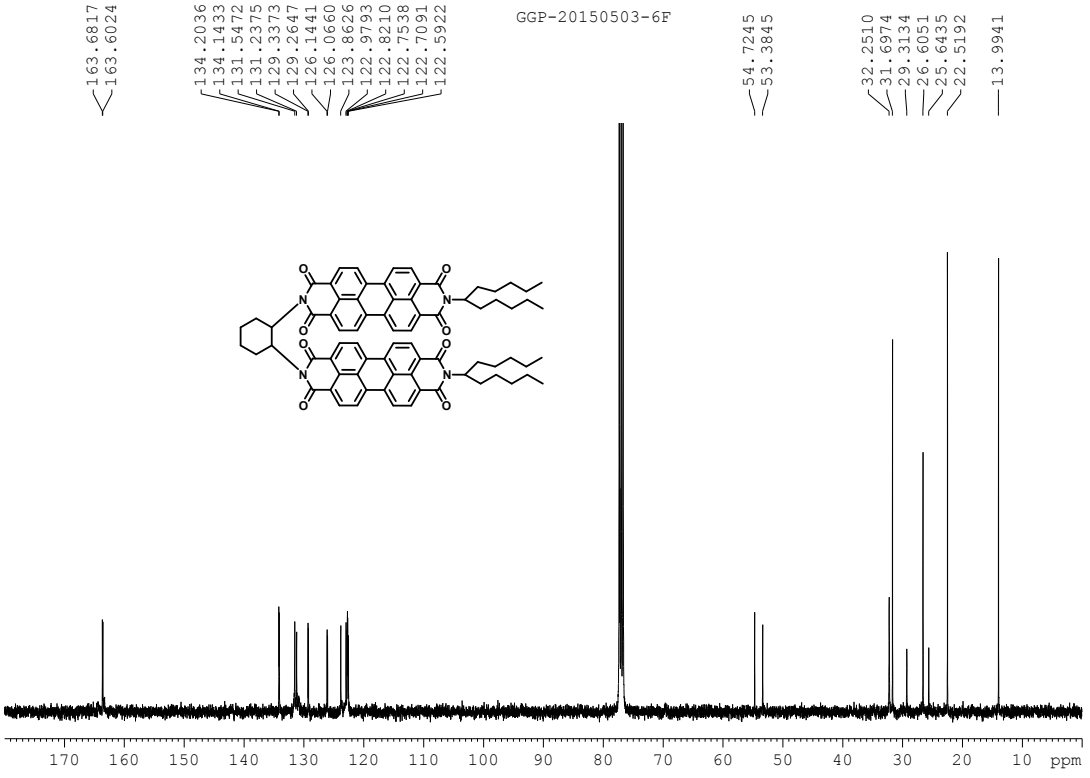
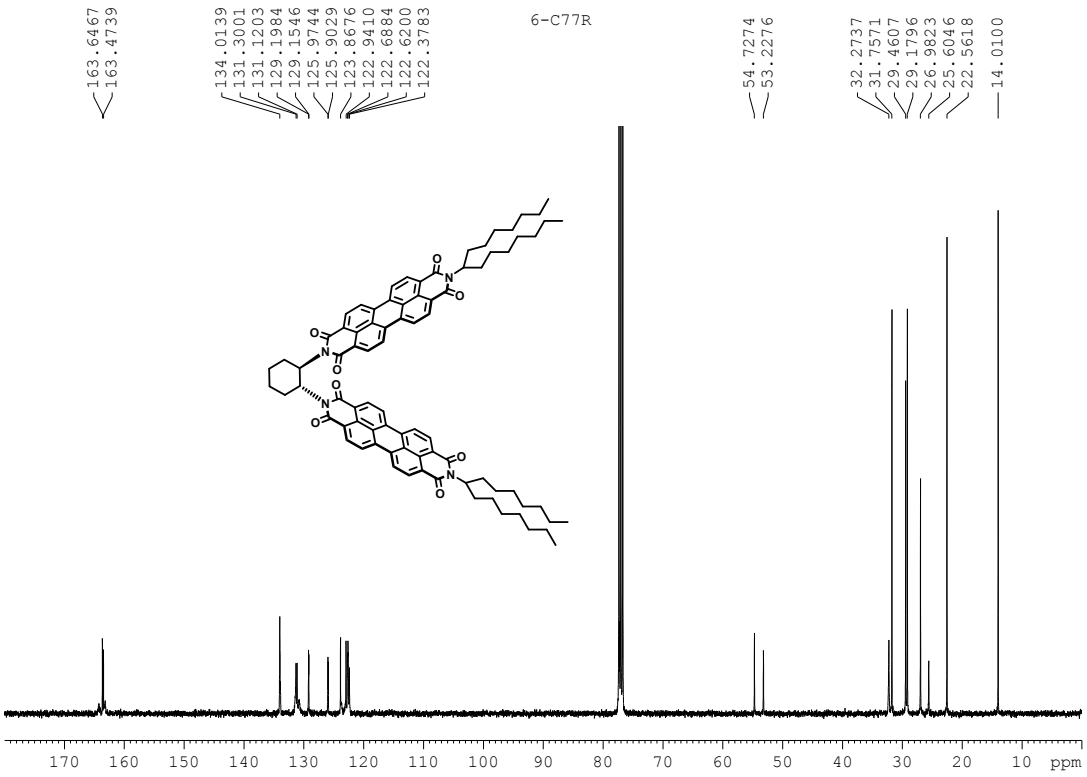


^{13}C NMR spectrum of **3a** in $CDCl_3$ (100 MHz, 25 ºC).



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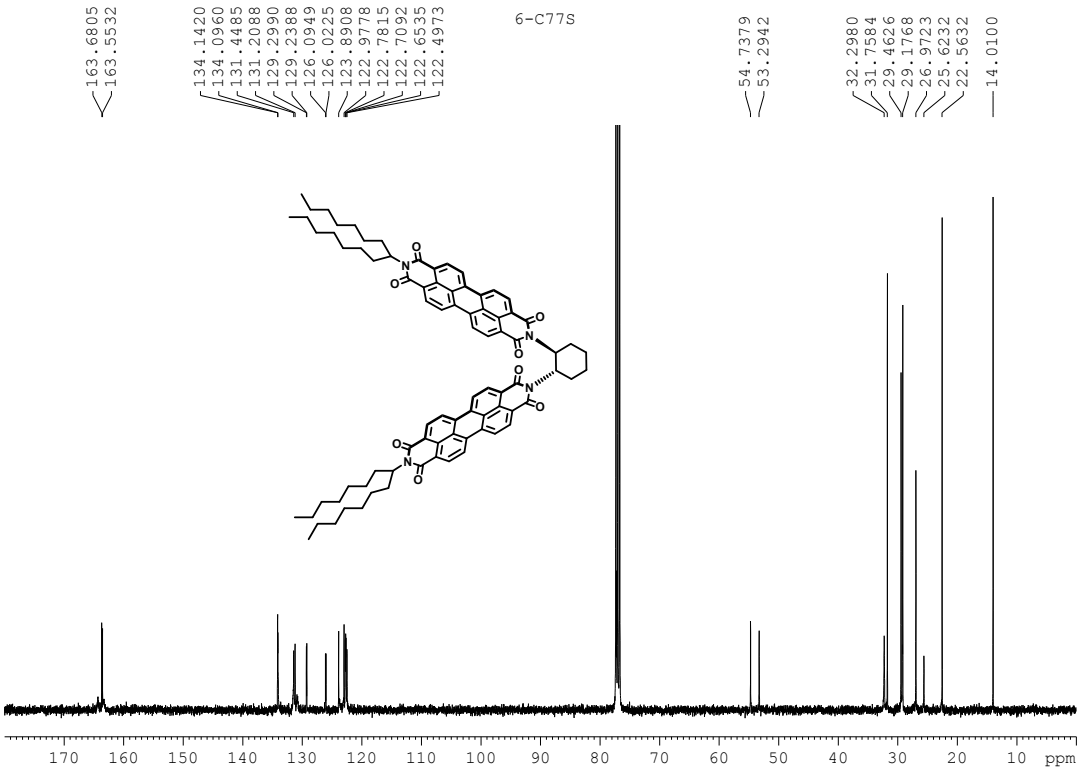

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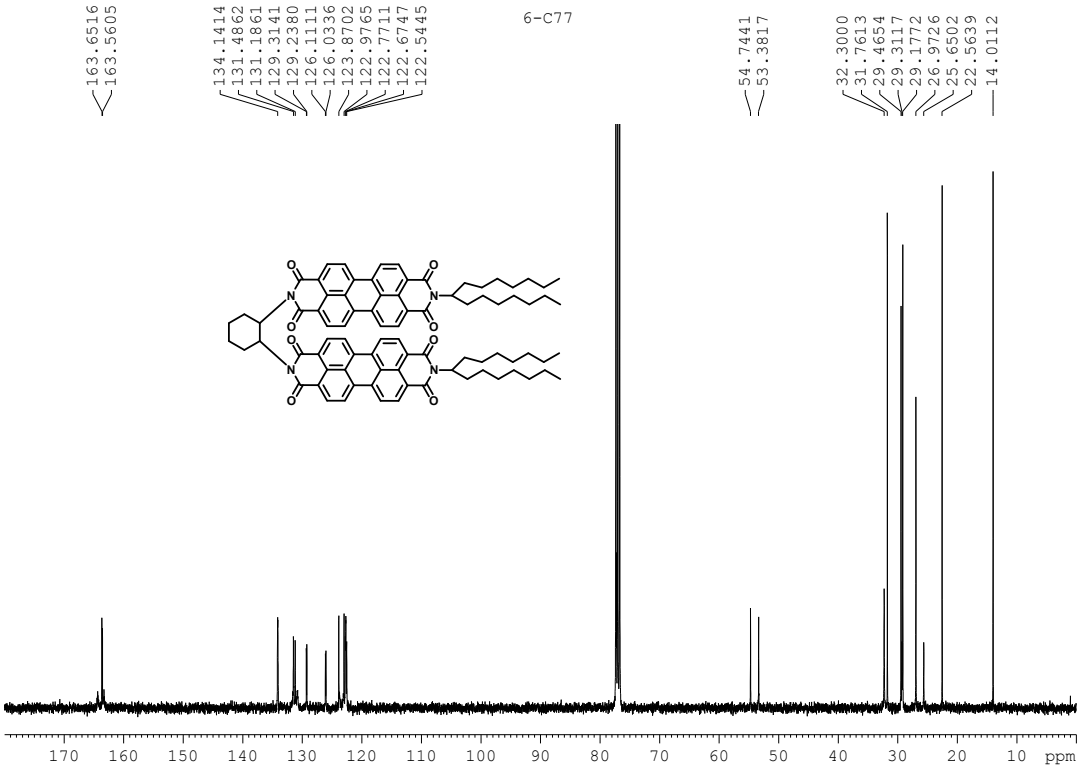

HRMS spectrum of **2a**.

MALDI(N),6fr,20141121

Analysis Info

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Sample Name		Instrument	solariX
Comment			

Acquisition Parameter

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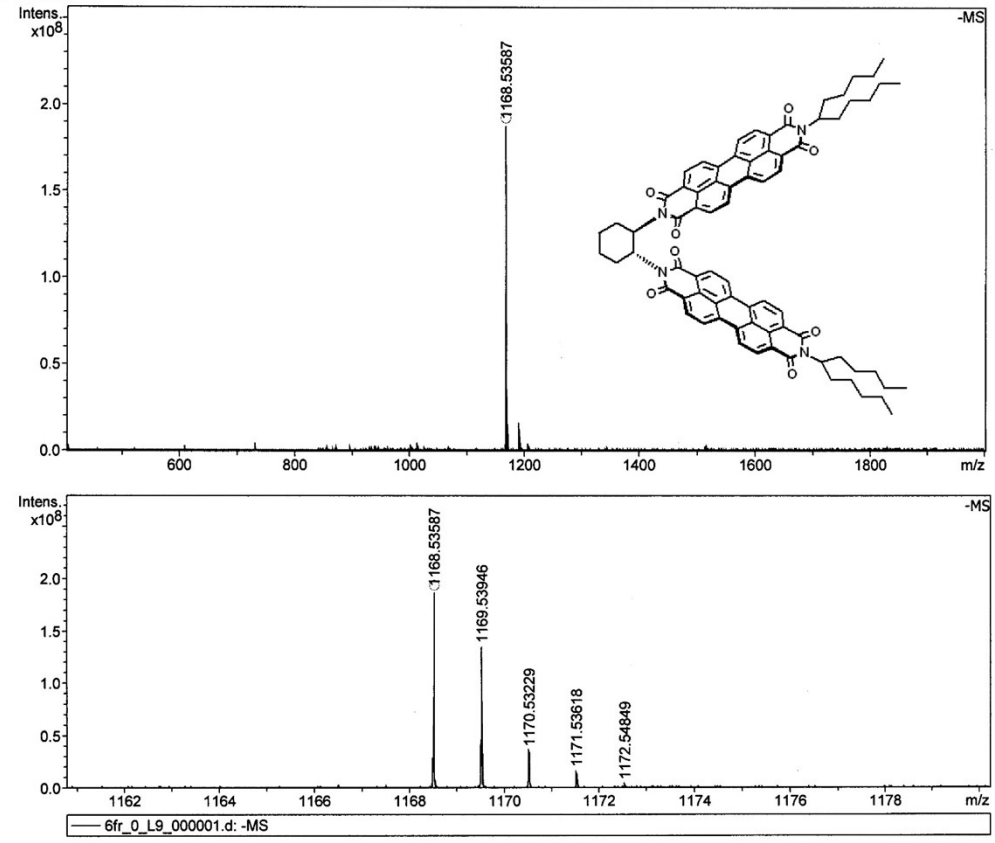
Ion Accumulation Time	0.300 sec				



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
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HRMS spectrum of **2b**.

MALDI(N),6fs,20141121

Analysis Info

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Sample Name		Instrument	solariX
Comment			

Acquisition Parameter

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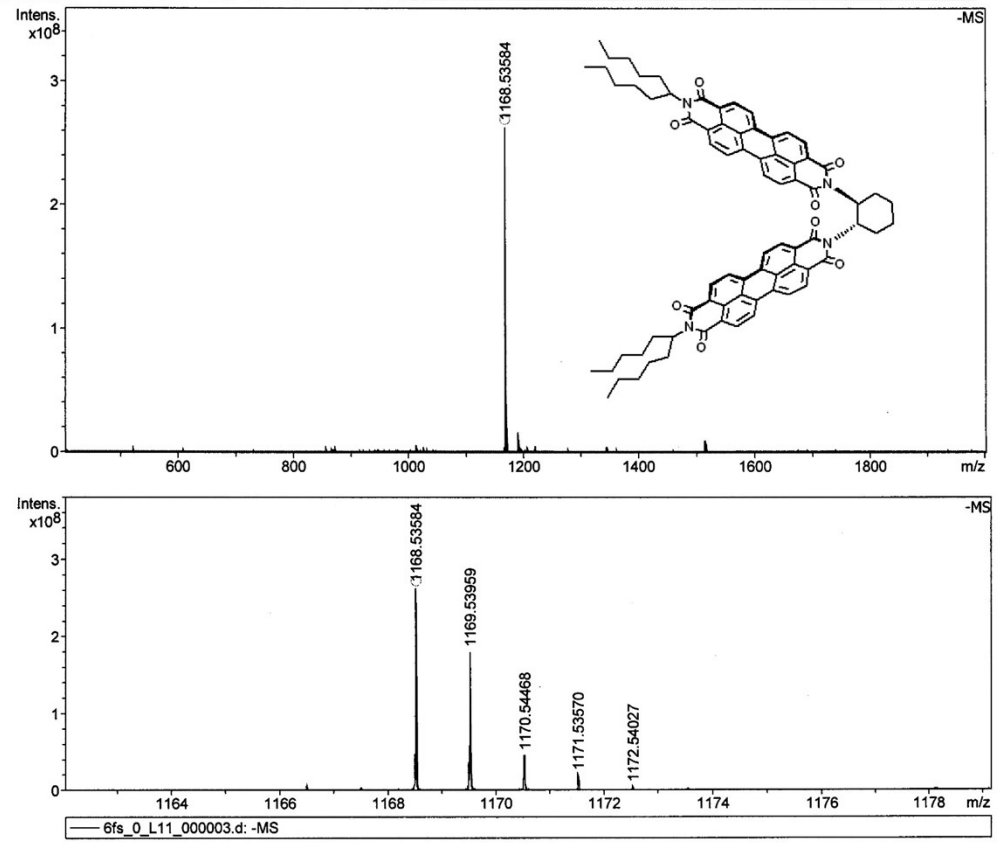
Broadband Low Mass	404.2 m/z	No. of Laser Shots	10	Data Processing Size	2097152
Broadband High Mass	2000.0 m/z	Laser Power	18.0 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.001 sec	Laser Shot Frequency	0.020 sec		
Ion Accumulation Time	0.300 sec				



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1168.535841	1	C76H72N4O8	100.00	1168.535564	-0.2	-0.6	114.7	43.0	odd	ok

HRMS spectrum of **2c**.

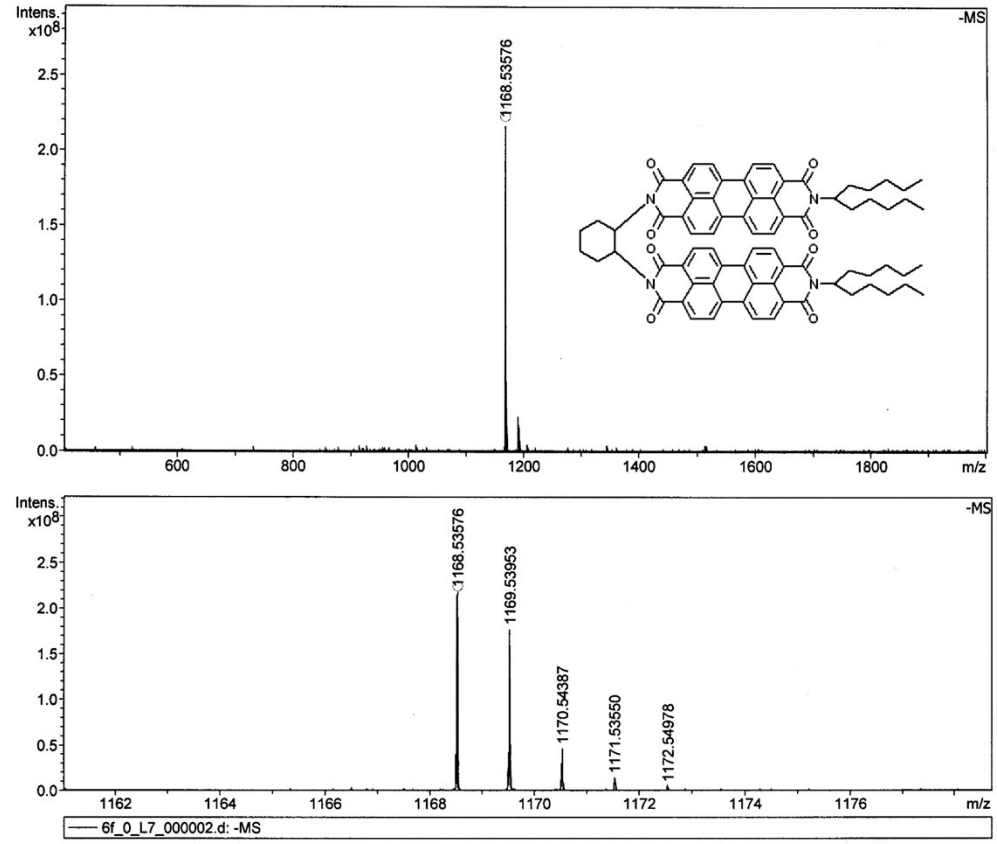
MALDI(N),6f,20141121

Analysis Info

Analysis Name	D:\Data\MALDI\2014\1121\6f_0_L7_000002.d	Acquisition Date	11/21/2014 6:35:48 PM
Method	MALDI_P_100-3000	Operator	
Sample Name		Instrument	solariX
Comment			

Acquisition Parameter

Acquisition Mode	Single MS	Acquired Scans	6	Calibration Date	Fri Nov 21 06:21:04 2014
Polarity	Negative	No. of Cell Fills	1	Data Acquisition Size	1048576
Broadband Low Mass	404.2 m/z	No. of Laser Shots	10	Data Processing Size	2097152
Broadband High Mass	2000.0 m/z	Laser Power	18.0 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.001 sec	Laser Shot Frequency	0.020 sec		
Ion Accumulation Time	0.300 sec				



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1168.535758	1	C76H72N4O8	100.00	1168.535564	-0.2	-0.5	80.8	43.0	odd	ok

HRMS spectrum of **3a**.

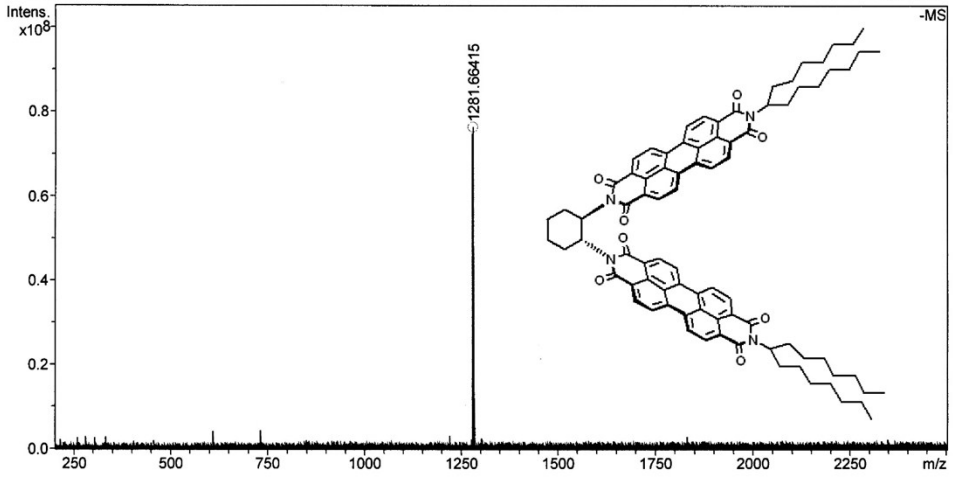
MALDI(N),6-C7R,20150819

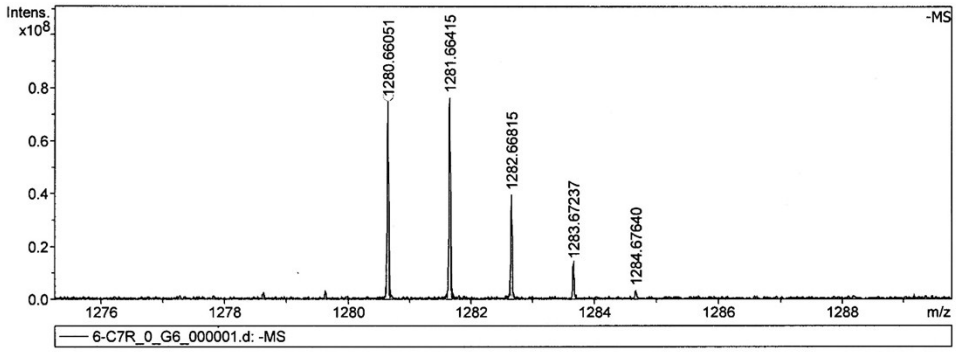
Analysis Info

Analysis Name	D:\Data\MALDI\2015\0819\6-C7R_0_G6_000001.d	Acquisition Date	8/19/2015 3:52:45 PM
Method	MALDI_N_100-900	Operator	
Sample Name		Instrument	solariX
Comment			

Acquisition Parameter

Acquisition Mode	Single MS	Acquired Scans	5	Calibration Date	Wed Aug 19 03:46:07
Polarity	Negative	No. of Cell Fills	1	Data Acquisition Size	2048576
Broadband Low Mass	202.1 m/z	No. of Laser Shots	10	Data Processing Size	2097152
Broadband High Mass	2500.0 m/z	Laser Power	24.6 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.001 sec	Laser Shot Frequency	0.020 sec		
Ion Accumulation Time	0.300 sec				





Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1280.660514	1	C84H88N4O8	100.00	1280.660764	-0.2	-0.2	41.6	43.0	odd	ok

HRMS spectrum of **3b**.

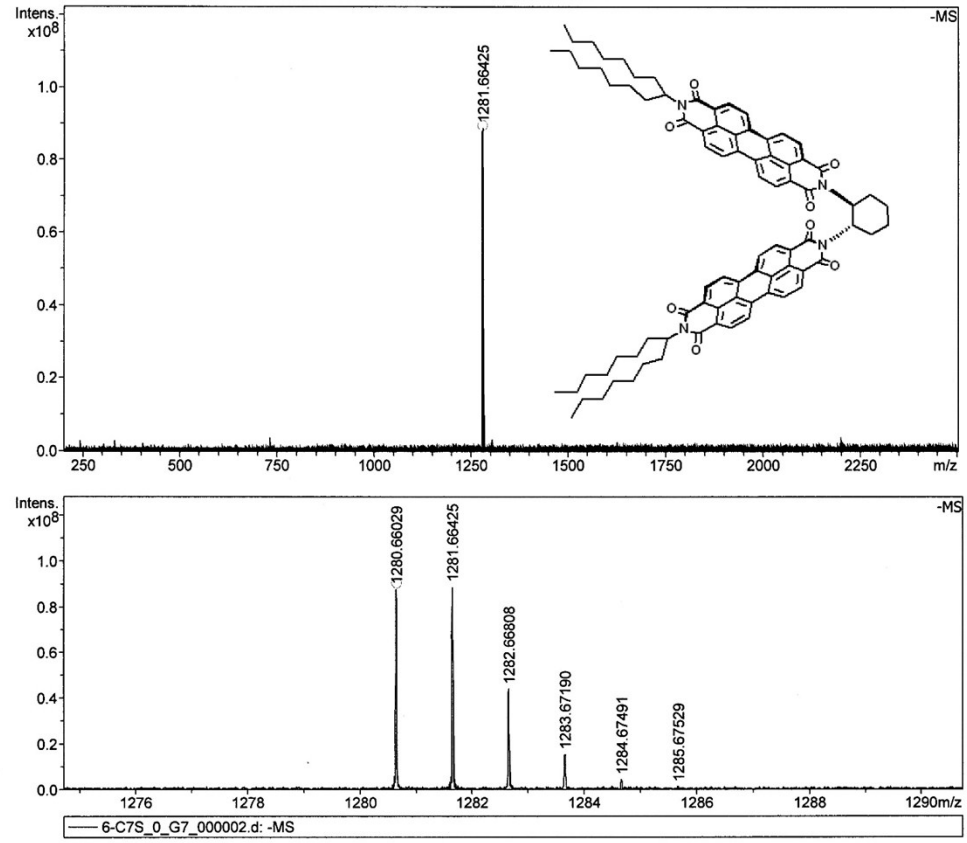
MALDI(N),6-C7S,20150819

Analysis Info

Analysis Name	D:\Data\MALDI\2015\0819\6-C7S_0_G7_000002.d	Acquisition Date	8/19/2015 3:55:29 PM
Method	MALDI_N_100-900	Operator	
Sample Name		Instrument	solariX
Comment			

Acquisition Parameter

Acquisition Mode	Single MS	Acquired Scans	5	Calibration Date	Wed Aug 19 03:46:07
Polarity	Negative	No. of Cell Fills	1	Data Acquisition Size	2048576
Broadband Low Mass	202.1 m/z	No. of Laser Shots	10	Data Processing Size	2097152
Broadband High Mass	2500.0 m/z	Laser Power	24.0 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.001 sec	Laser Shot Frequency	0.020 sec		
Ion Accumulation Time	0.300 sec				



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1280.660290	1	C84H88N4O8	100.00	1280.660764	0.4	-0.1	35.1	43.0	odd	ok

HRMS spectrum of **3c**.

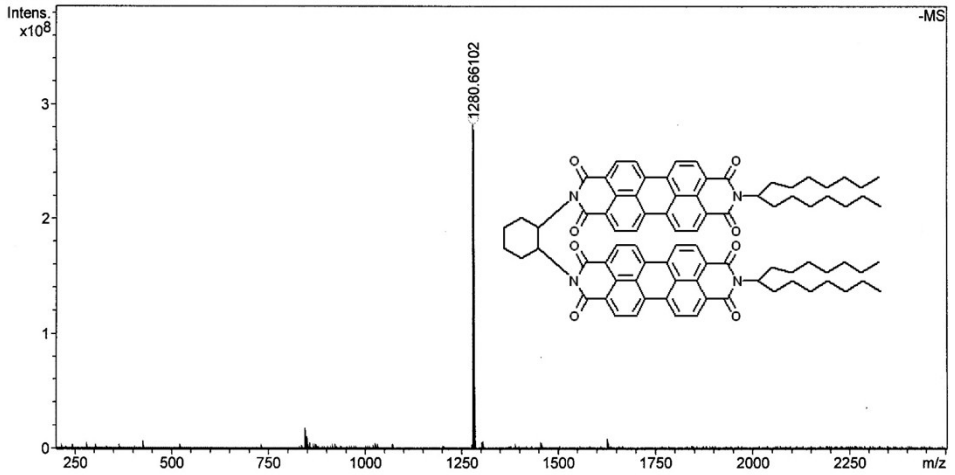
MALDI(N),6-C7,20150819

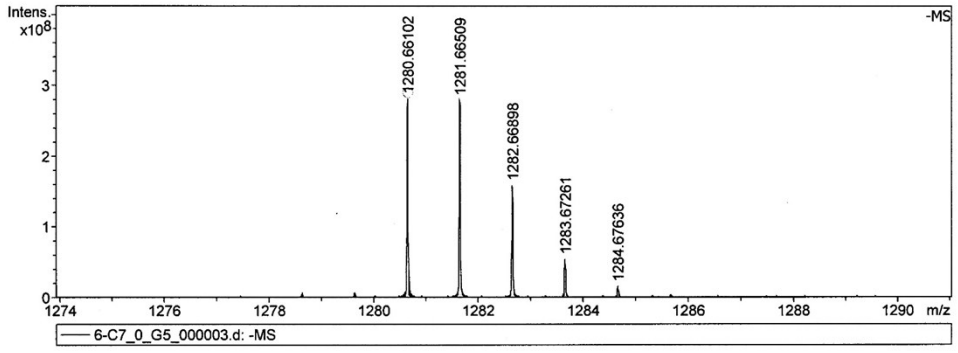
Analysis Info

Analysis Name	D:\Data\MALDI\2015\0819\6-C7_0_G5_000003.d	Acquisition Date	8/19/2015 3:50:00 PM
Method	MALDI_N_100-900	Operator	
Sample Name		Instrument	solariX
Comment			

Acquisition Parameter

Acquisition Mode	Single MS	Acquired Scans	5	Calibration Date	Wed Aug 19 03:46:07
Polarity	Negative	No. of Cell Fills	1	Data Acquisition Size	2048576
Broadband Low Mass	202.1 m/z	No. of Laser Shots	10	Data Processing Size	2097152
Broadband High Mass	2500.0 m/z	Laser Power	25.4 lp	Apodization	Sine-Bell Multiplication
Source Accumulation	0.001 sec	Laser Shot Frequency	0.020 sec		
Ion Accumulation Time	0.300 sec				





Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1280.661022	1	C84H88N4O8	100.00	1280.660764	0.2	-0.8	55.8	43.0	odd	ok