Supporting Information for

Perpendicularly entangled perylene diimides for high performance electron transport materials

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Photophysical Properties

Table S1

Compounds	2a	2b	2c	2d	2e	2f	4a	4b
T_m [°C][a]	---	---	339	289	169	---	---	---

[a] Melting point determined by DSC measurement with a scan rate of 10 °C/min.

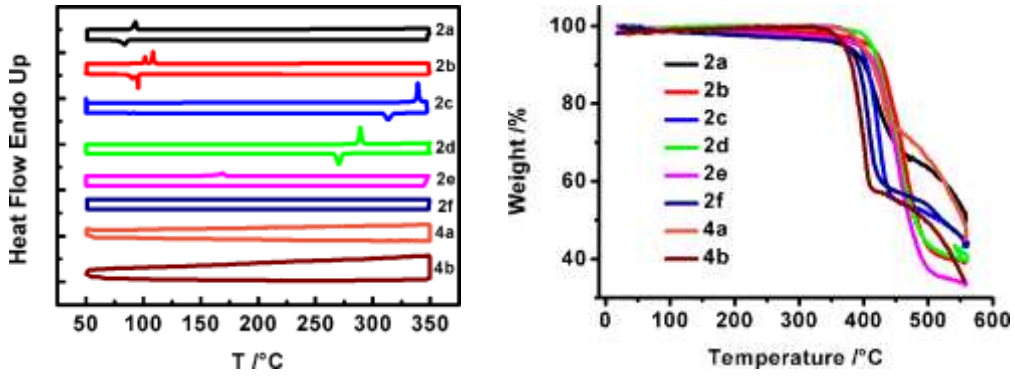


Fig. S1 DSCs and TGAs of all compounds

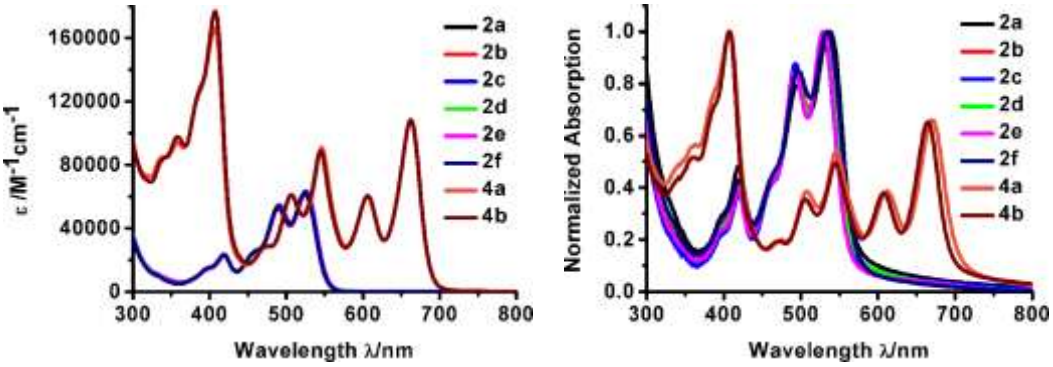


Fig. S2 UVs in chloroform solution and in film of all compounds

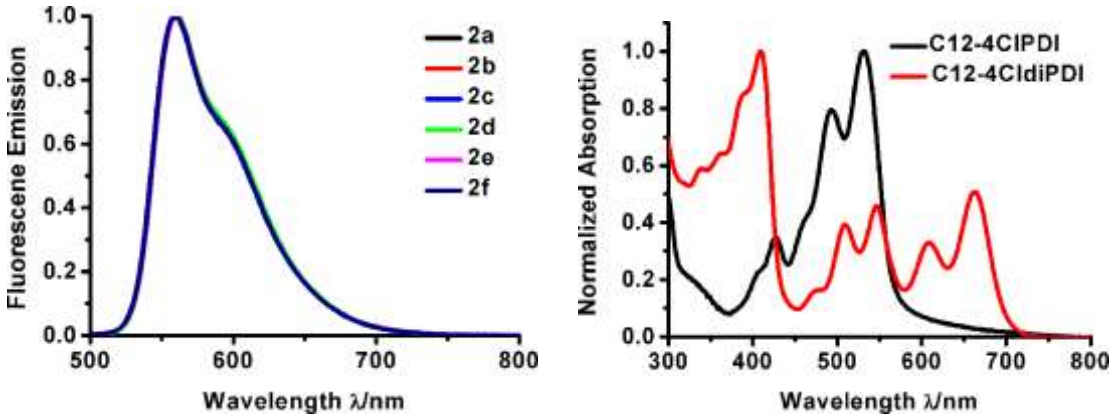


Fig. S3 Fluorescence spectra of 2a-2f and thin film absorption spectra of parent compounds

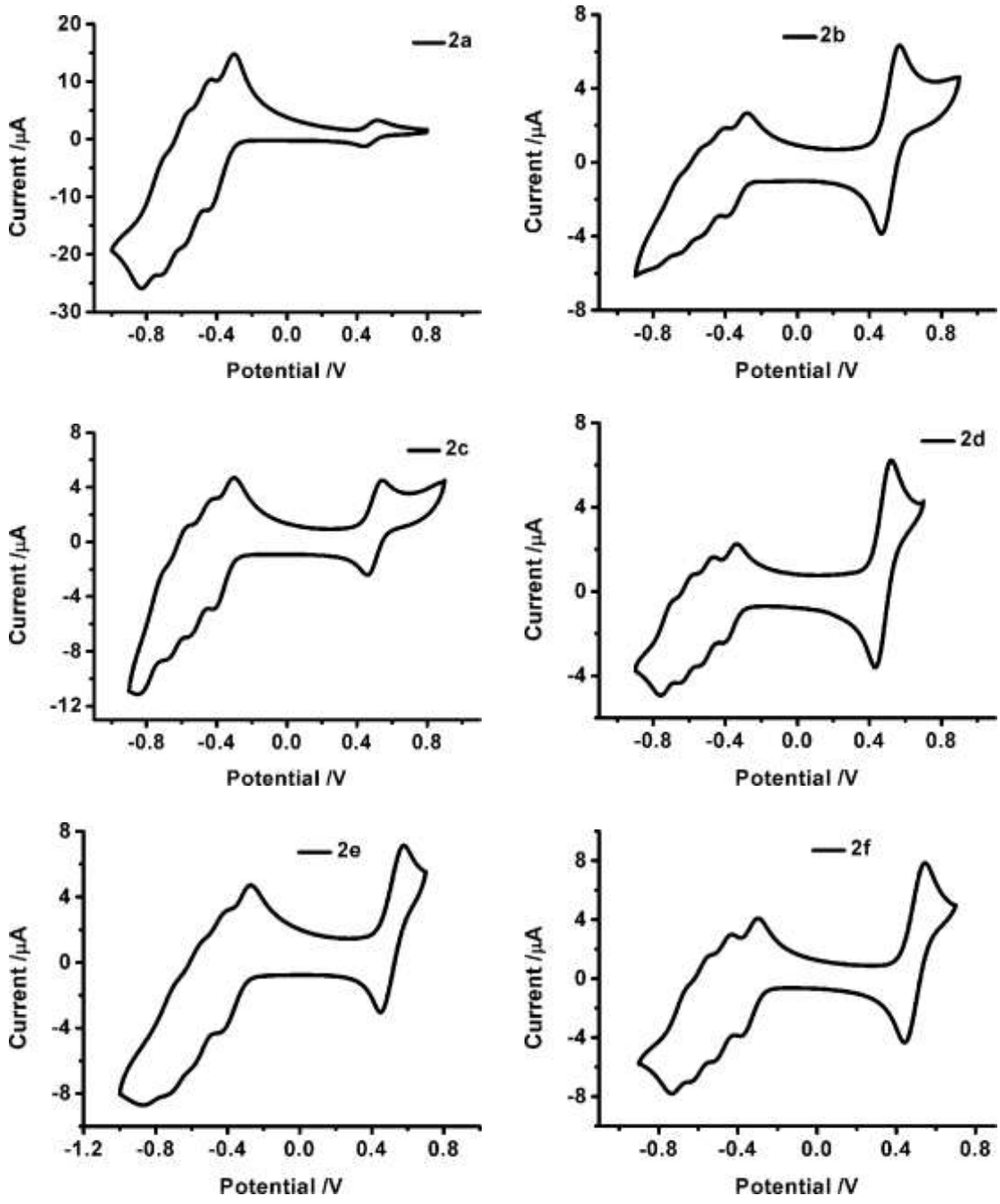


Fig. S4 CVs of compounds 2a-2f

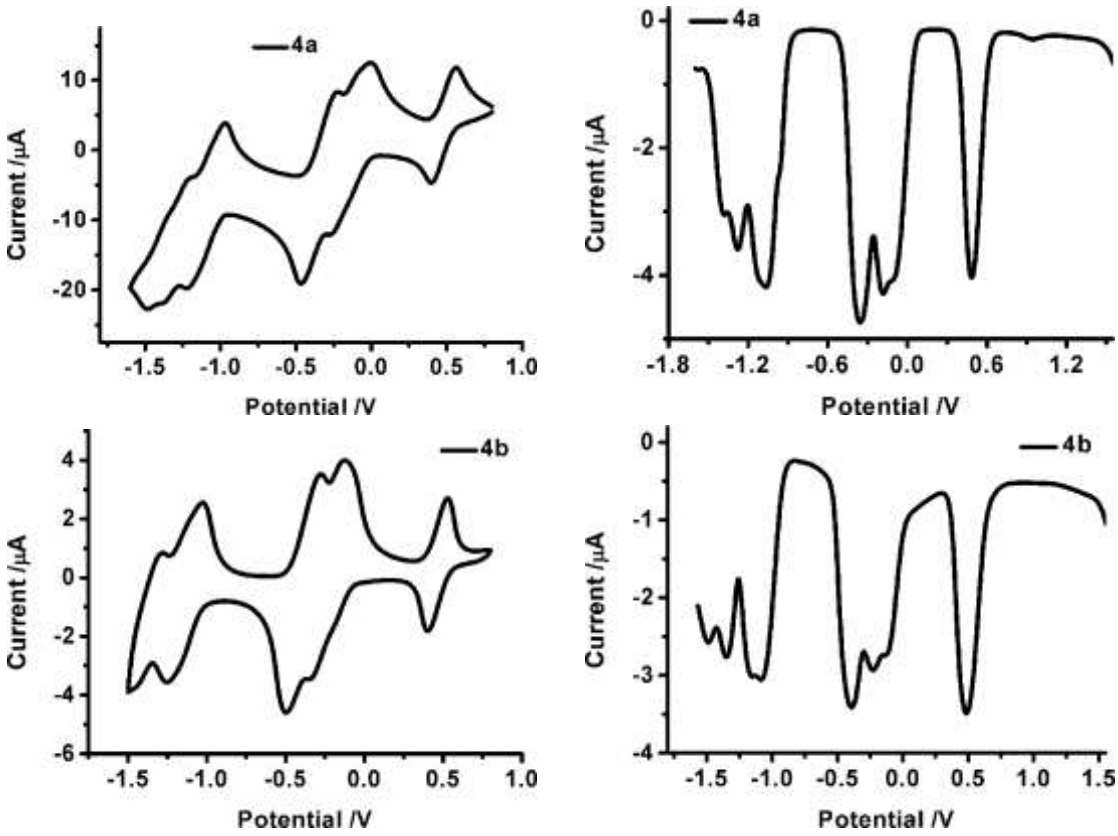


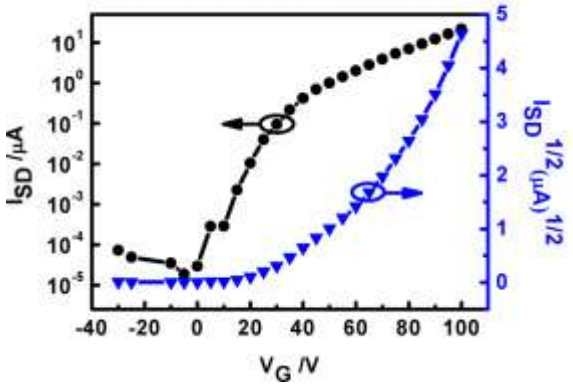
Fig. S5 CVs and DPVs of compounds 4a-4b

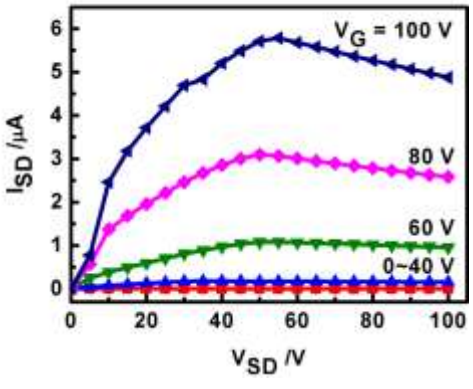
OTFT Properties

Table S2. The thin-film transistor properties of PDI dimers **2a-2f**, and diPDI dimers **4a-4b**

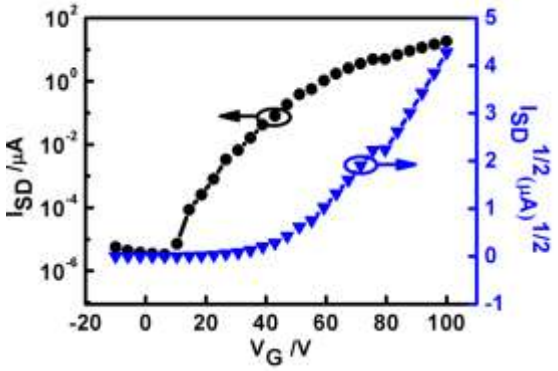
Compounds	$T_{annealing}$ [°C]	μ [$cm^2 V^{-1} s^{-1}$]	$I_{on/off}$	V_T [V]
2a	180	0.013	2.0×10^4	46
	220	0.043	9.0×10^5	44
	260	0.010	3.0×10^4	35
2b	180	0.16	5.0×10^6	45
	220	0.047	6.0×10^6	20
	260	0.072	7.0×10^6	25
2c	180	6.8×10^{-4}	2.0×10^5	26
	220	1.1×10^{-3}	2.0×10^5	12
	260	8.2×10^{-4}	4.0×10^5	48
2d	180	0.014	3.0×10^4	36
	220	0.055	1.0×10^5	57
	260	0.013	1.0×10^4	38
2e	RT	1.8×10^{-4}	5.0×10^5	44
	80	1.5×10^{-3}	9.0×10^4	25
	120	1.8×10^{-4}	1.0×10^4	46
2f	180	7.3×10^{-4}	1.0×10^2	-25
	220	7.0×10^{-4}	7.0×10^1	-42
	260	6.3×10^{-4}	1.0×10^1	-74
4a	180	2.8×10^{-3}	2.0×10^5	1
	220	0.027	5.0×10^6	3
	260	0.048	4.0×10^4	3
4b	180	7.8×10^{-4}	3.0×10^4	12
	220	2.8×10^{-3}	9.0×10^4	15
	260	1.7×10^{-3}	4.0×10^5	8

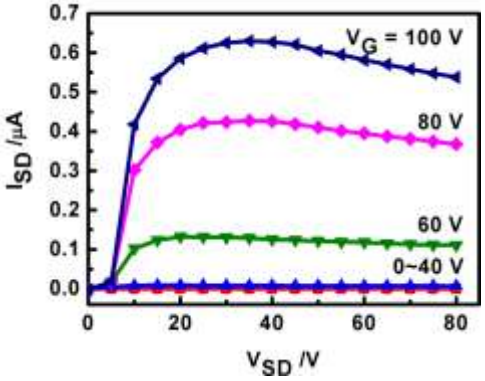
(a) Compound 2a $T_{annealing}$ = 220 °C



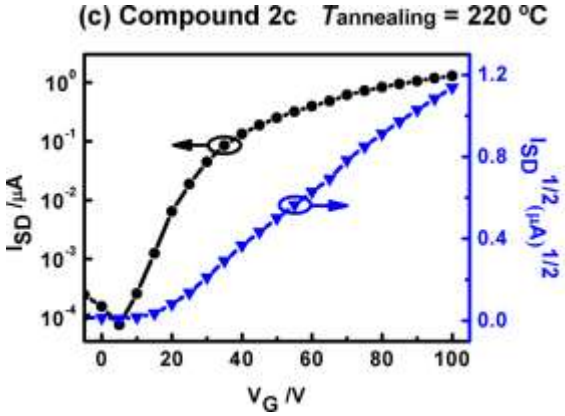


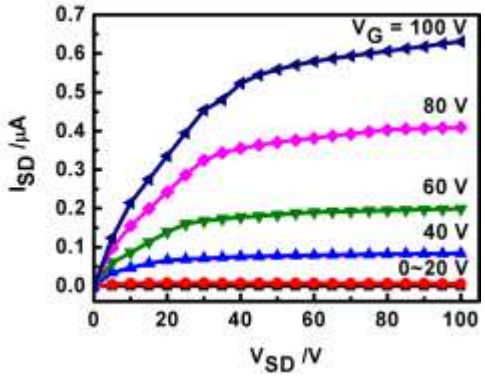
(b) Compound 2b $T_{annealing}$ = 180 °C



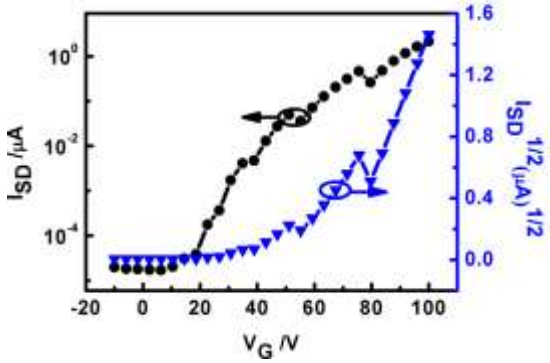


(c) Compound 2c $T_{annealing}$ = 220 °C

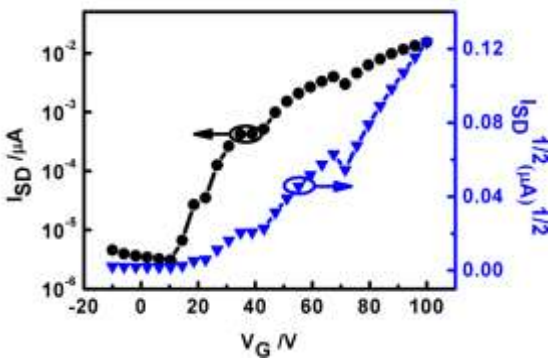




(d) Compound 2d $T_{annealing}$ = 220 °C



(e) Compound 2e $T_{annealing}$ = 80 °C



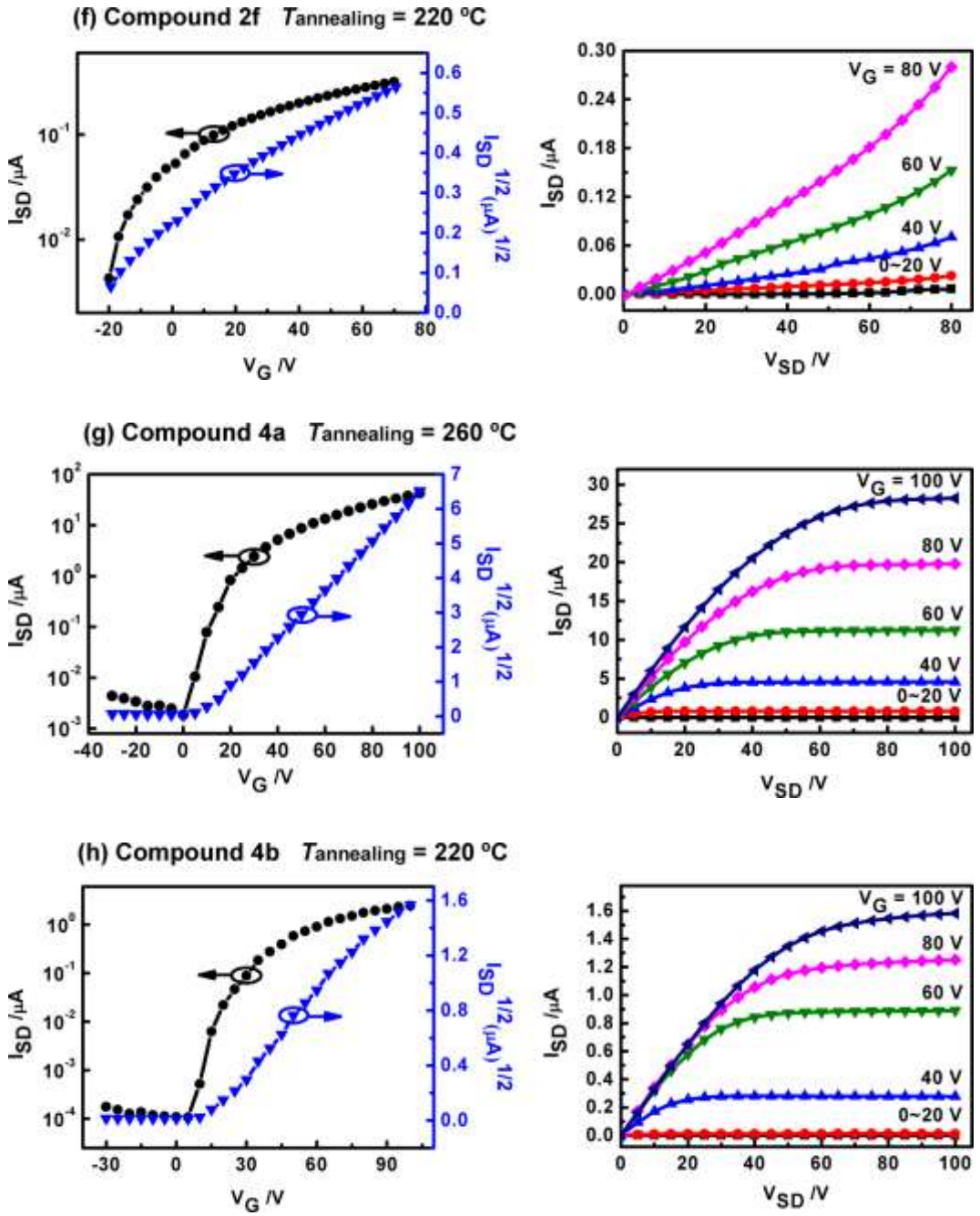


Fig. S6 Transfer and output characteristics for OTFT devices based on compounds 2a-2f and 4a-4b measured under ambient condition

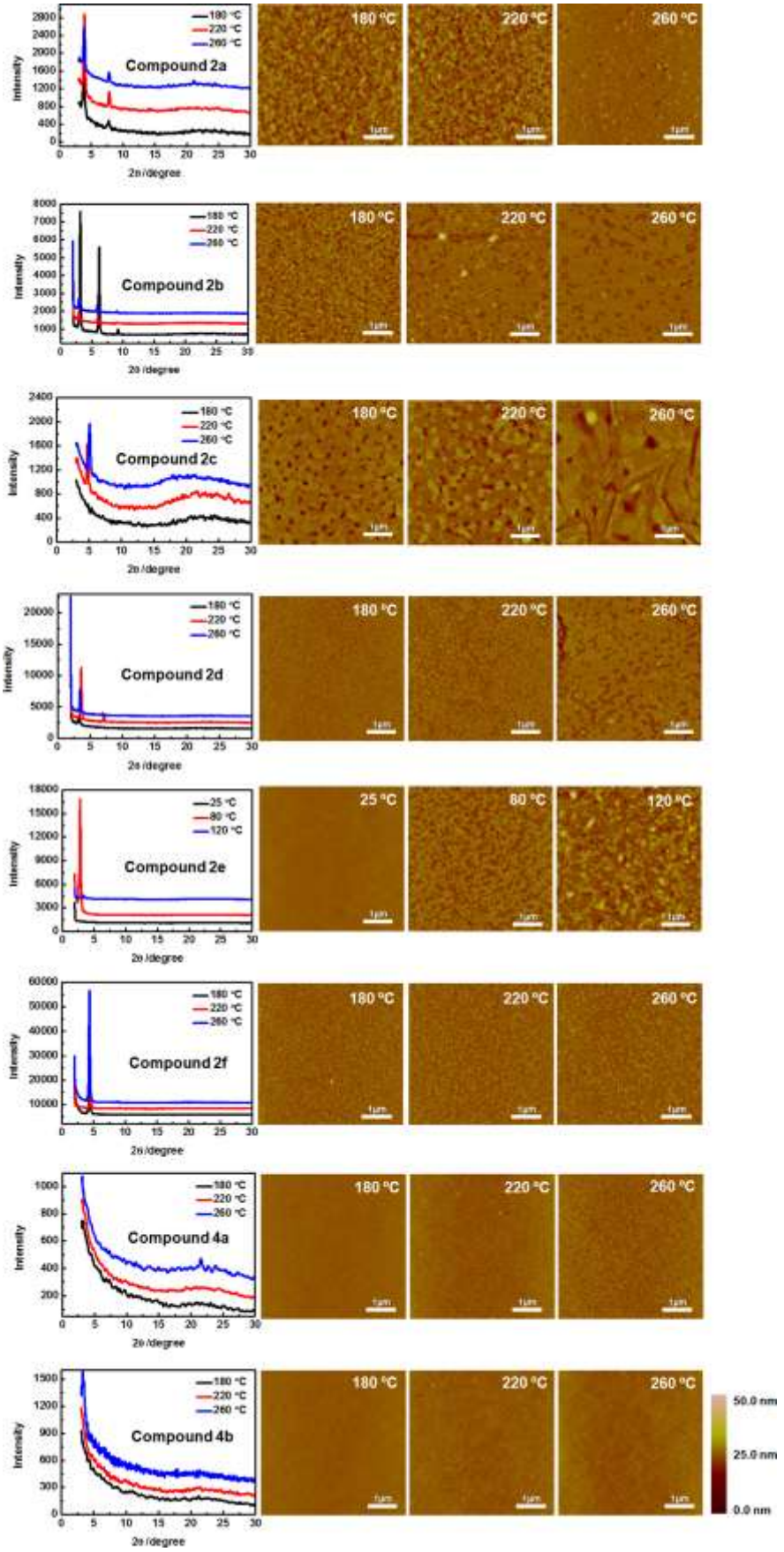
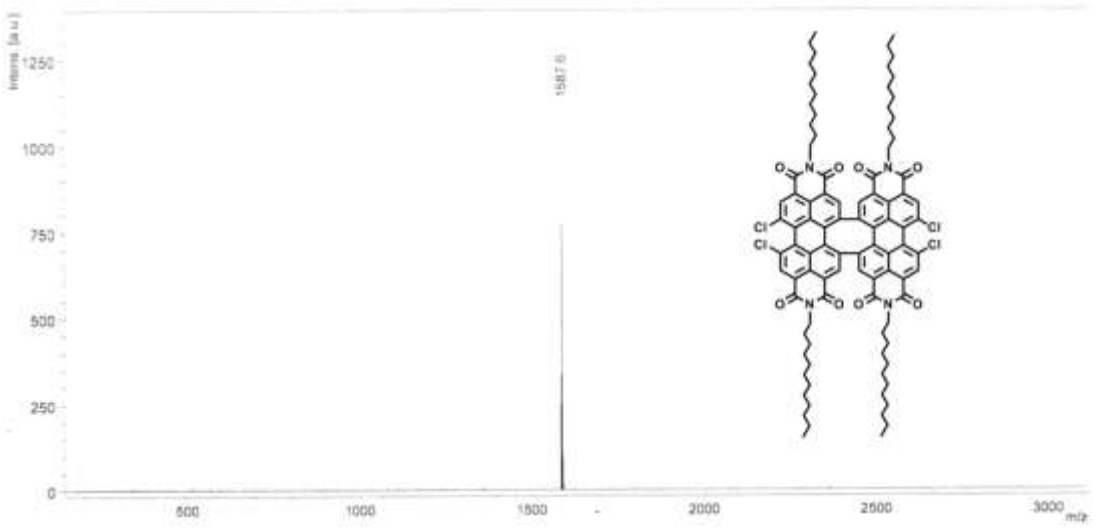


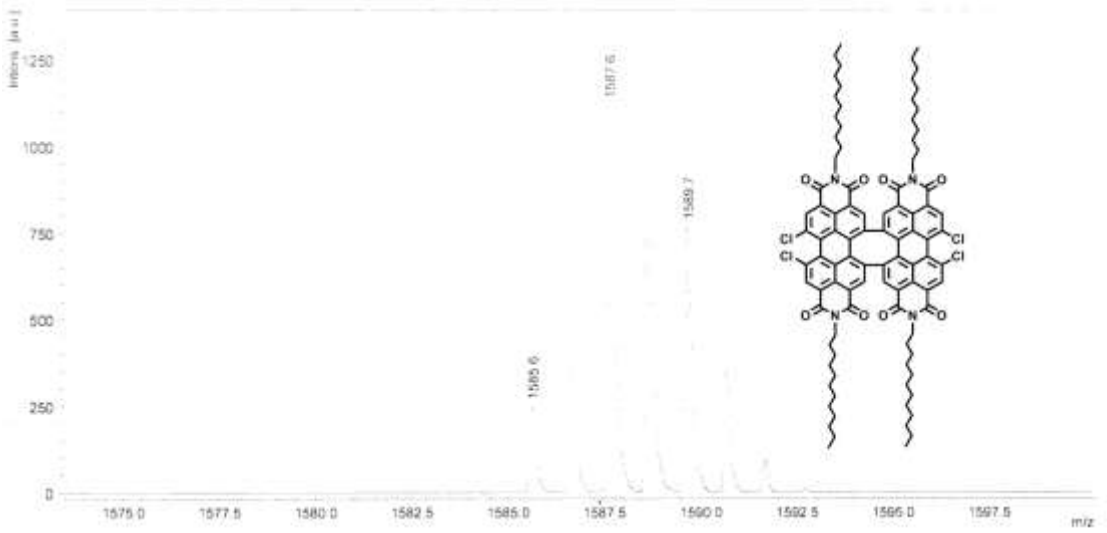
Fig. S7 Comparison of XRD and AFM images of thin films of 2a-2f and 4a-4b at different annealing temperatures

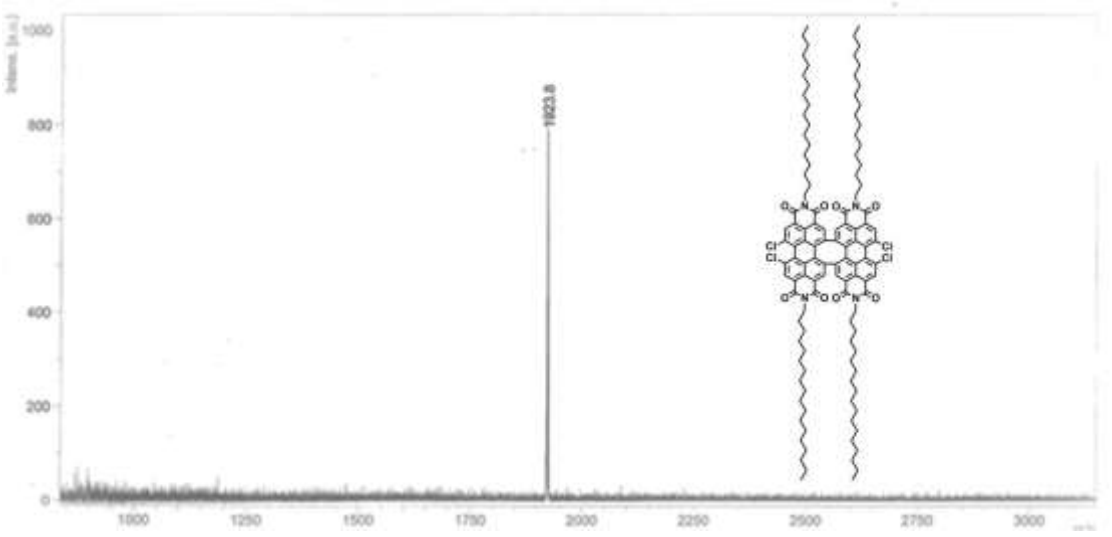
Table S3. The d-spacing values determined by XRD data

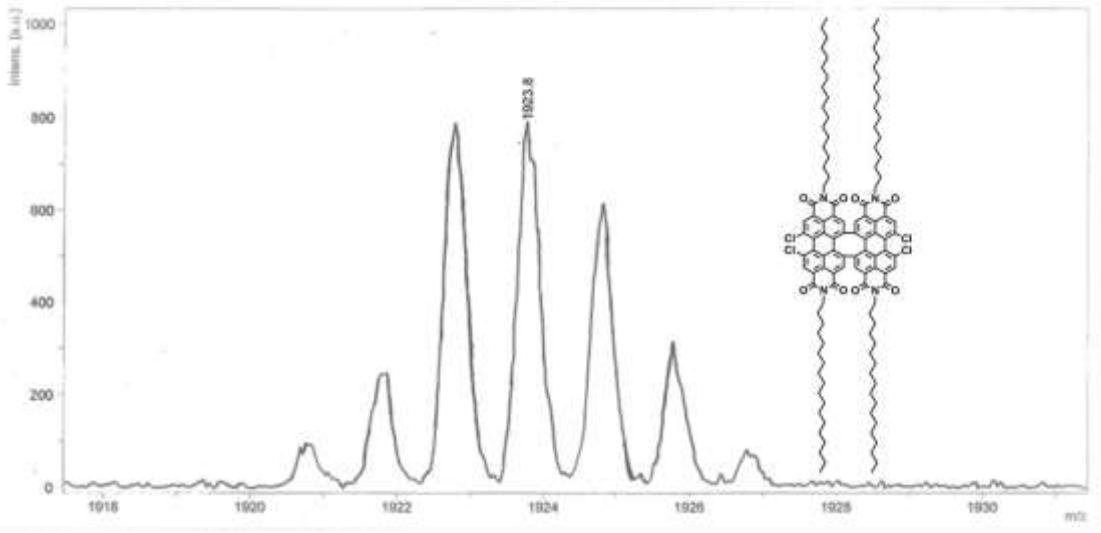
Compound	Linear Chain	*d*[Å]	Compound	Branched Chain	*d*[Å]
2a	**C12**	**22.5094**	**2c**	**C7,7**	**18.4677**
2b	**C18**	**27.7519**	**2d**	**C8,6**	**24.1176**
2f	**PEG**	**20.1629**	**2e**	**C10,12**	**31.0637**

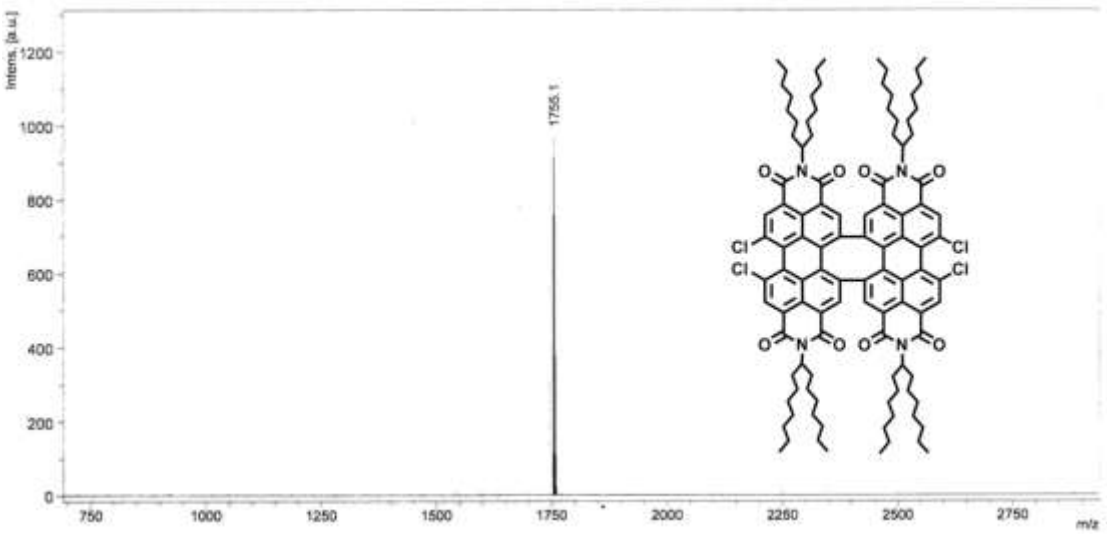
MS of the Compounds 2a-2f, 4a-4b







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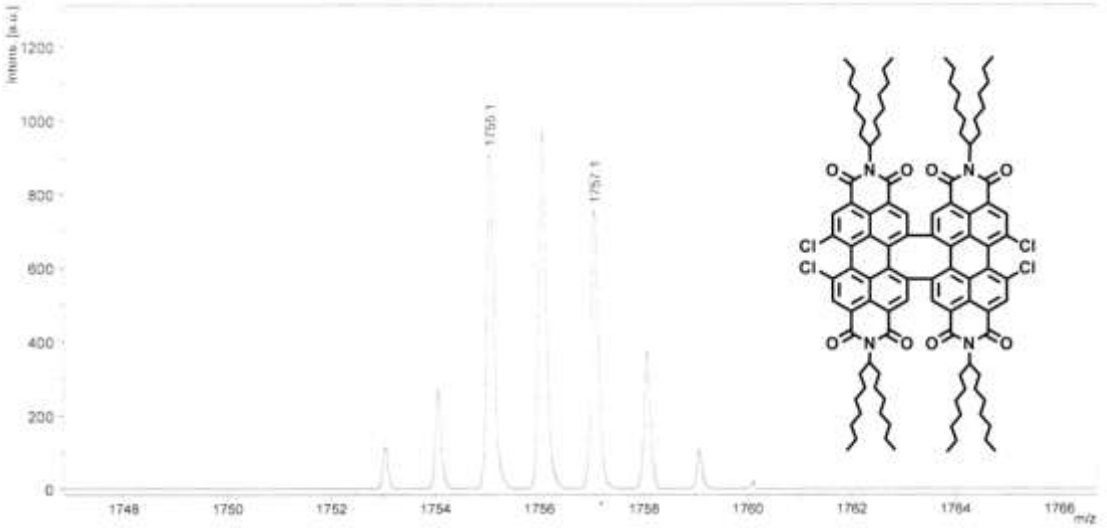
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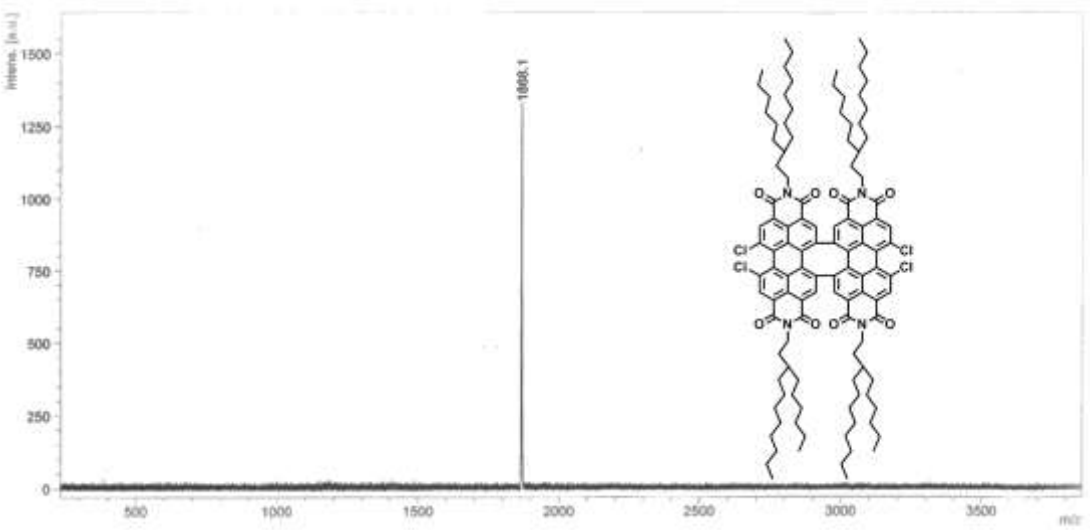

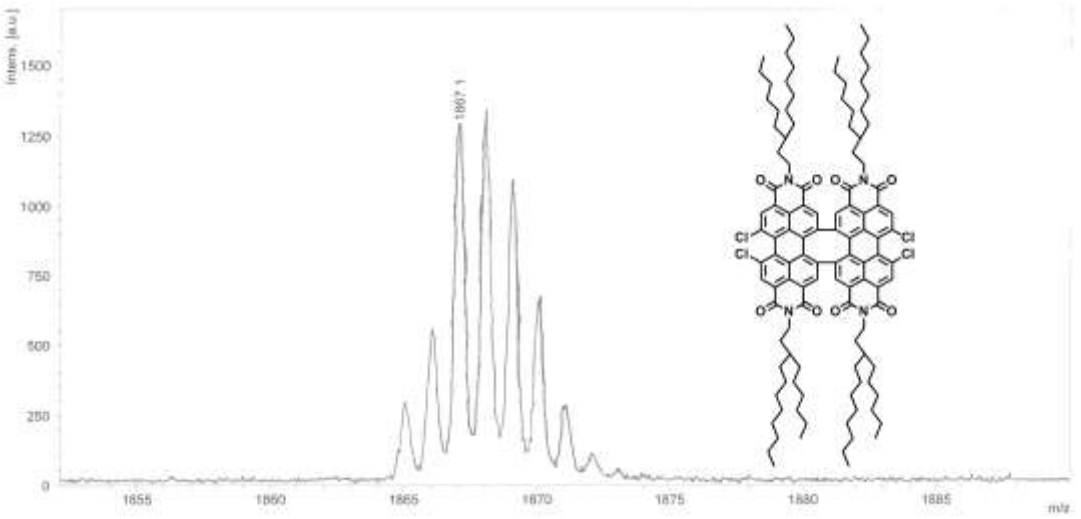

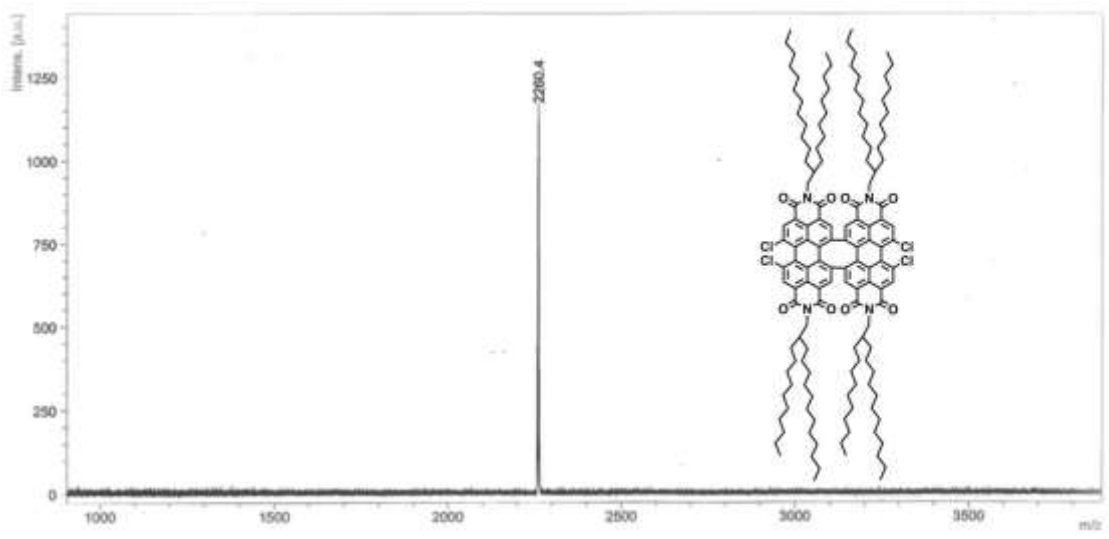

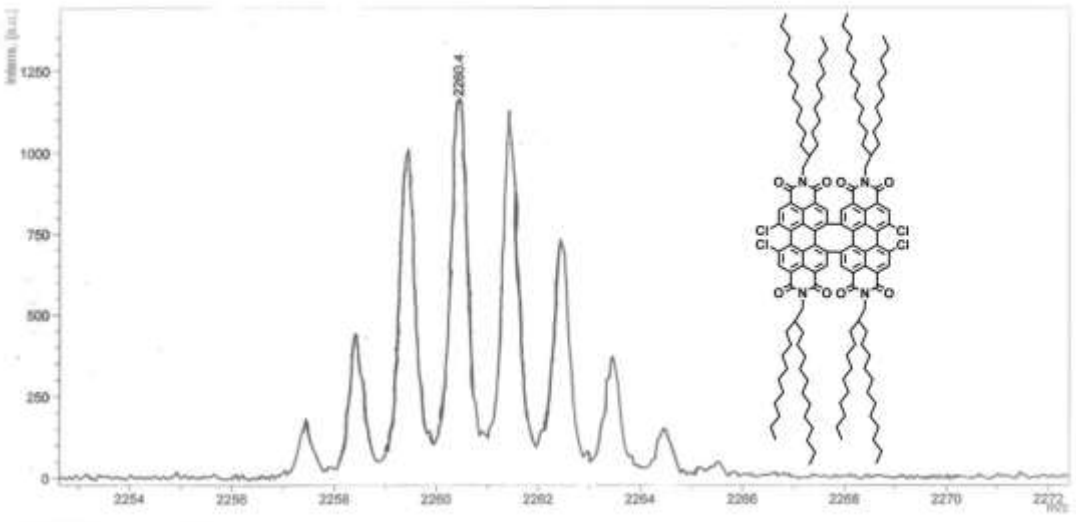

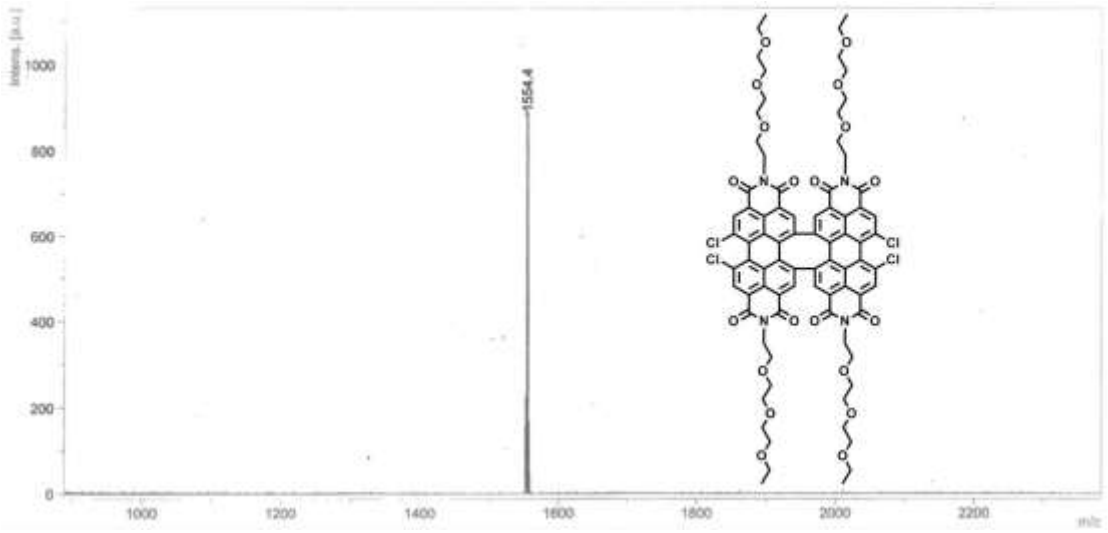
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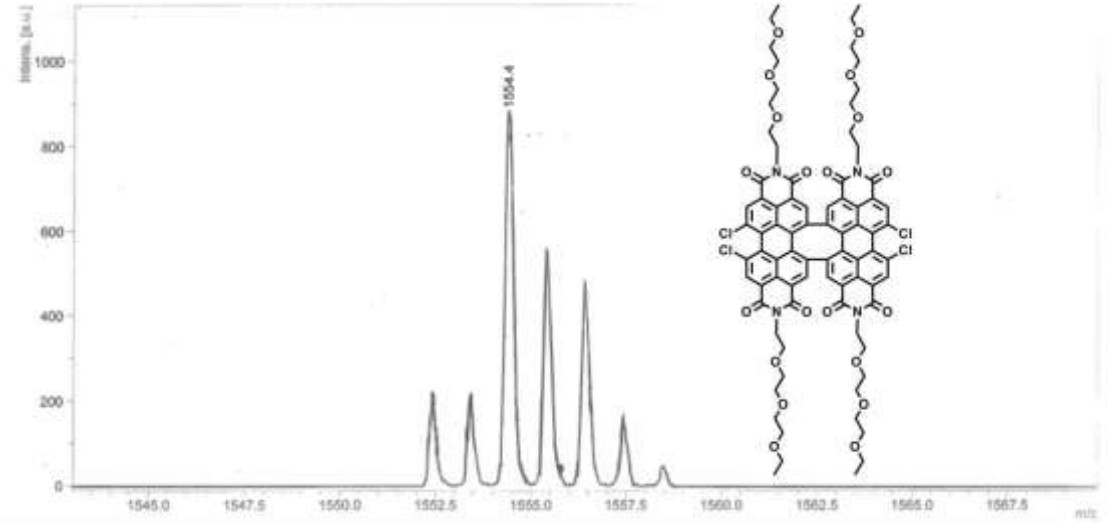
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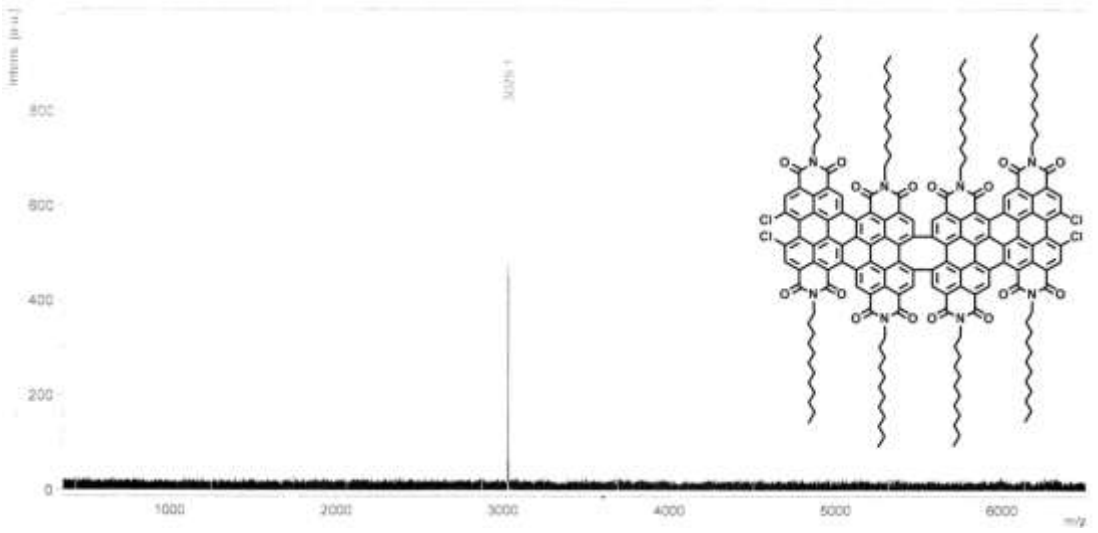
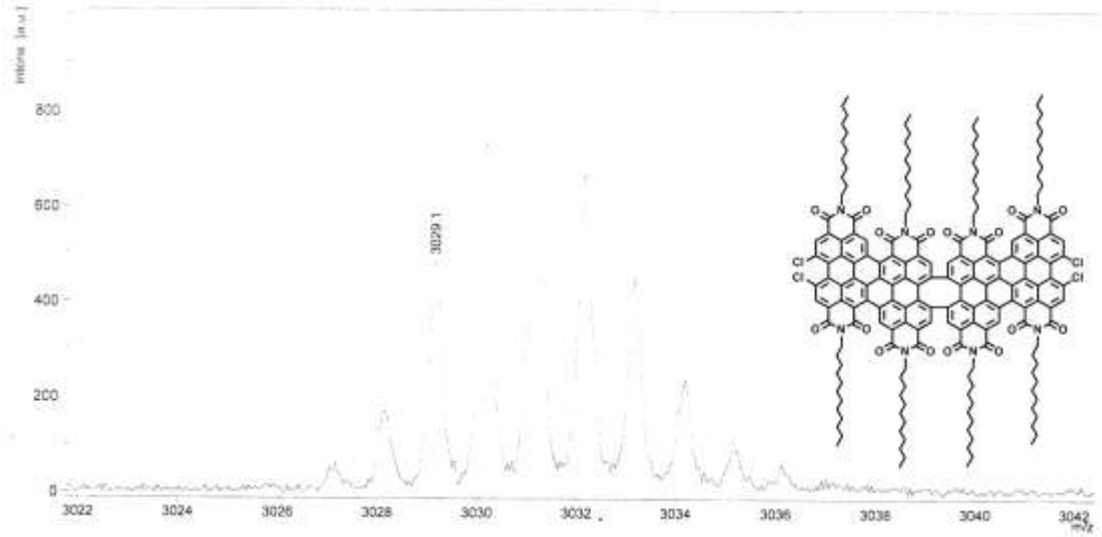
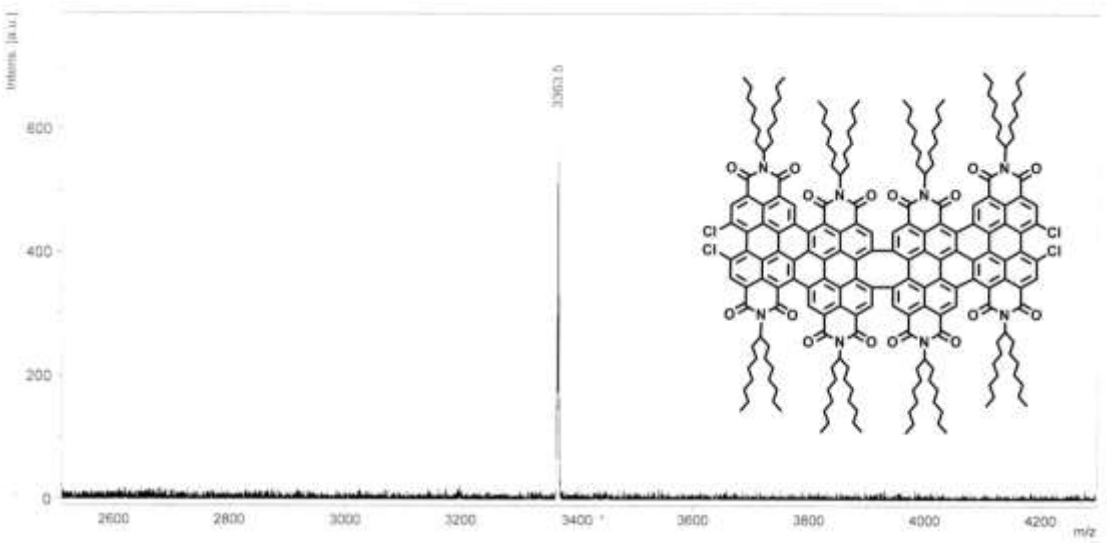
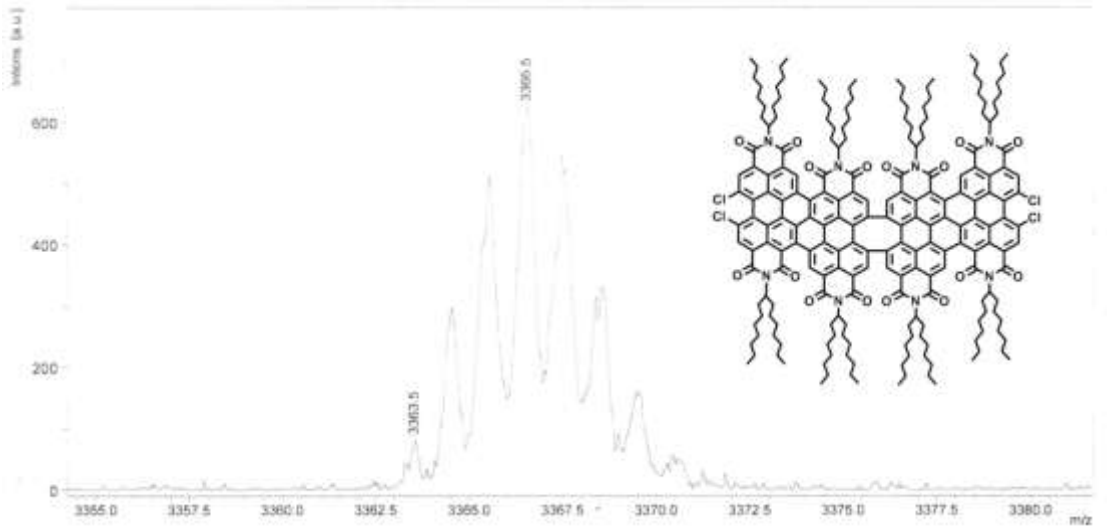


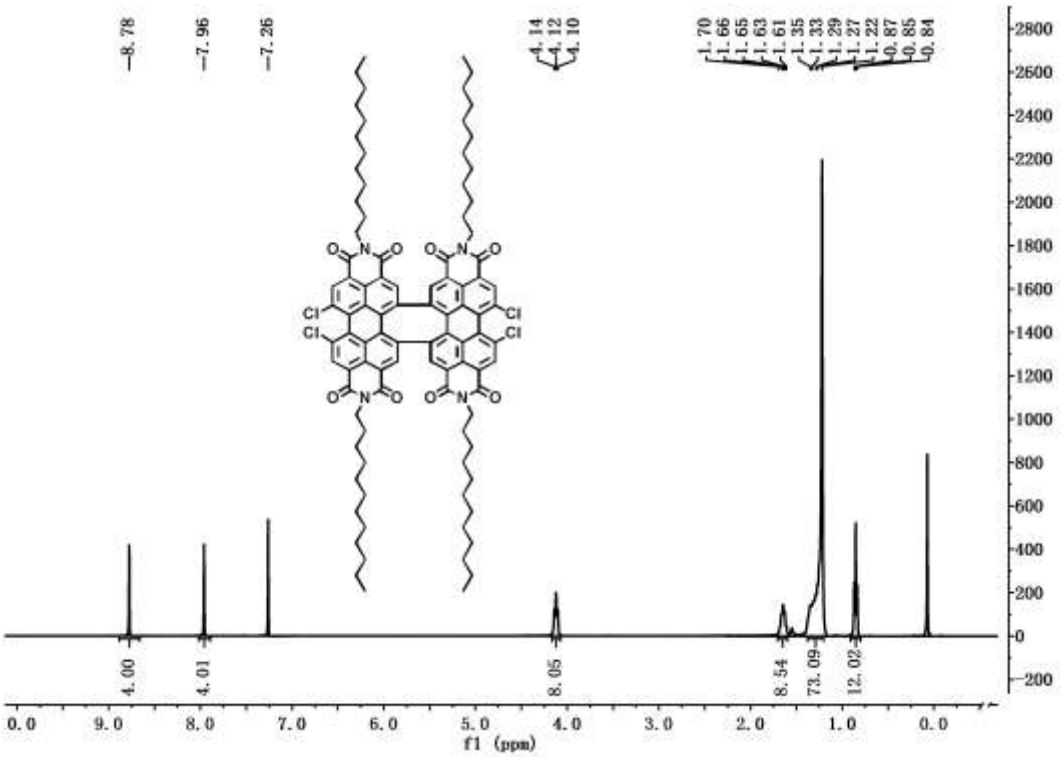




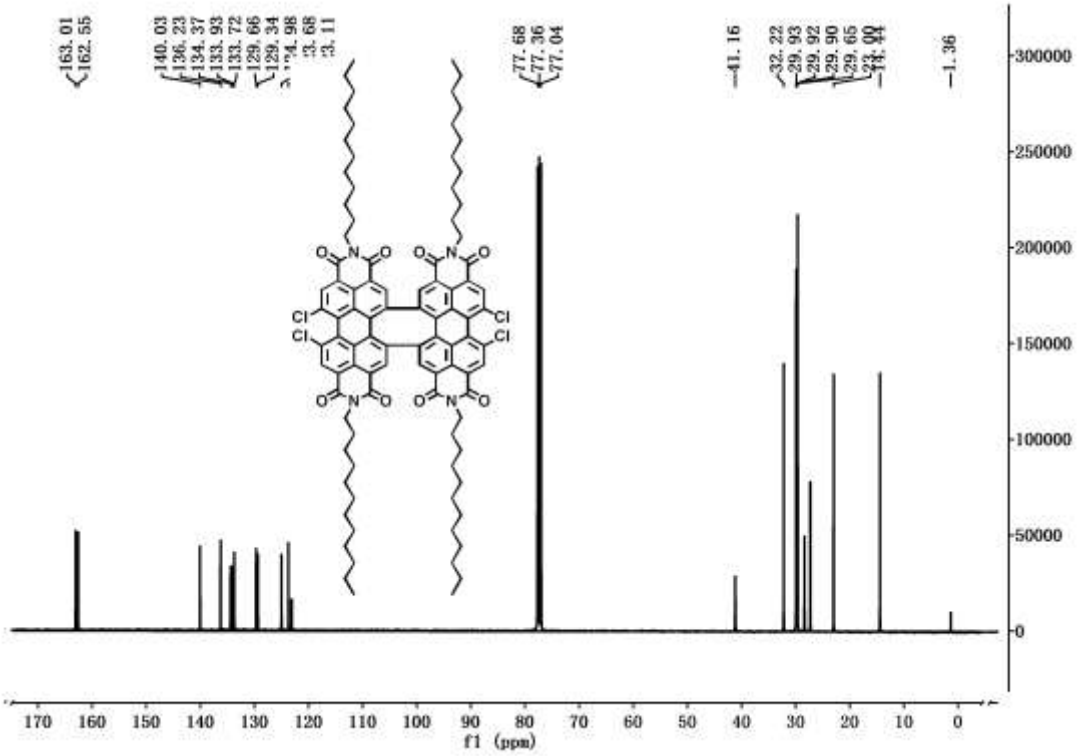


^{1}H NMR and ^{13}C NMR Spectra in $CDCl_3$

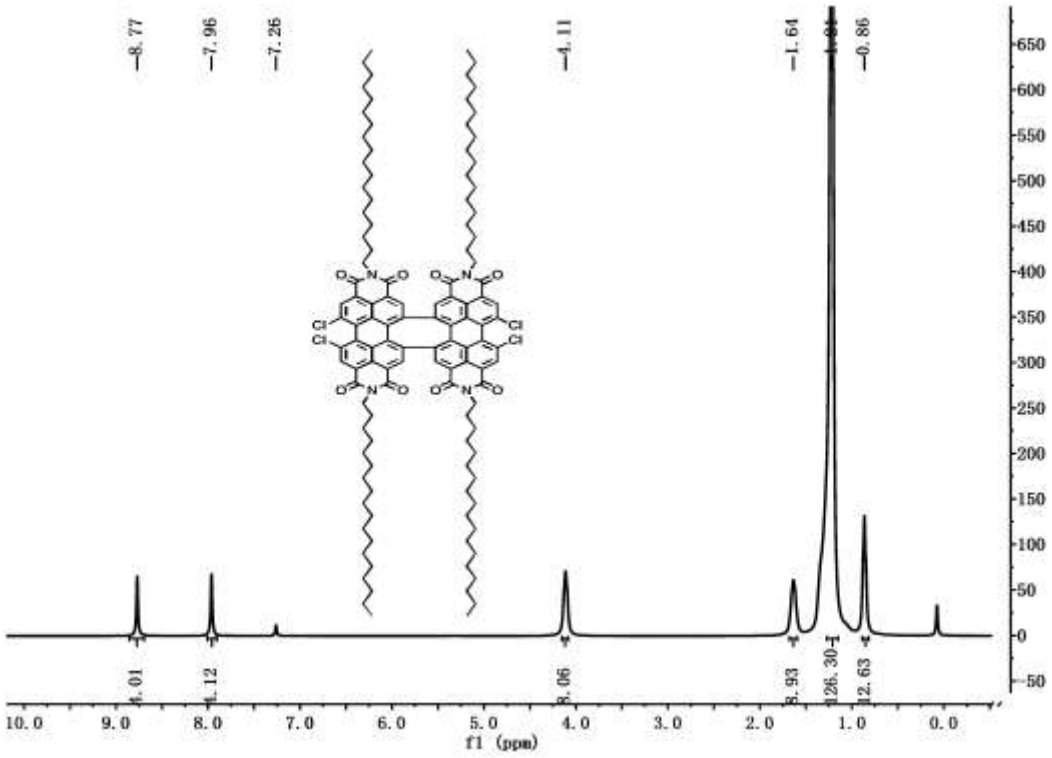
^{1}H NMR Spectrum of 2a at 400 MHz



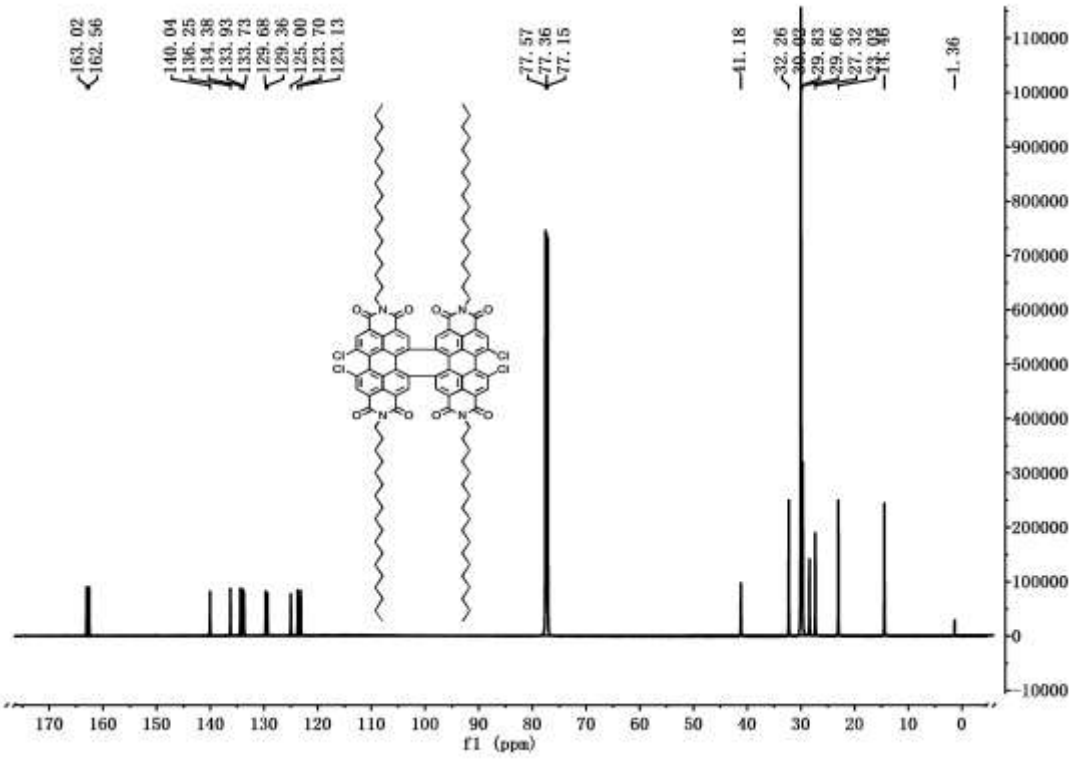
^{13}C NMR Spectrum of 2a at 100 MHz



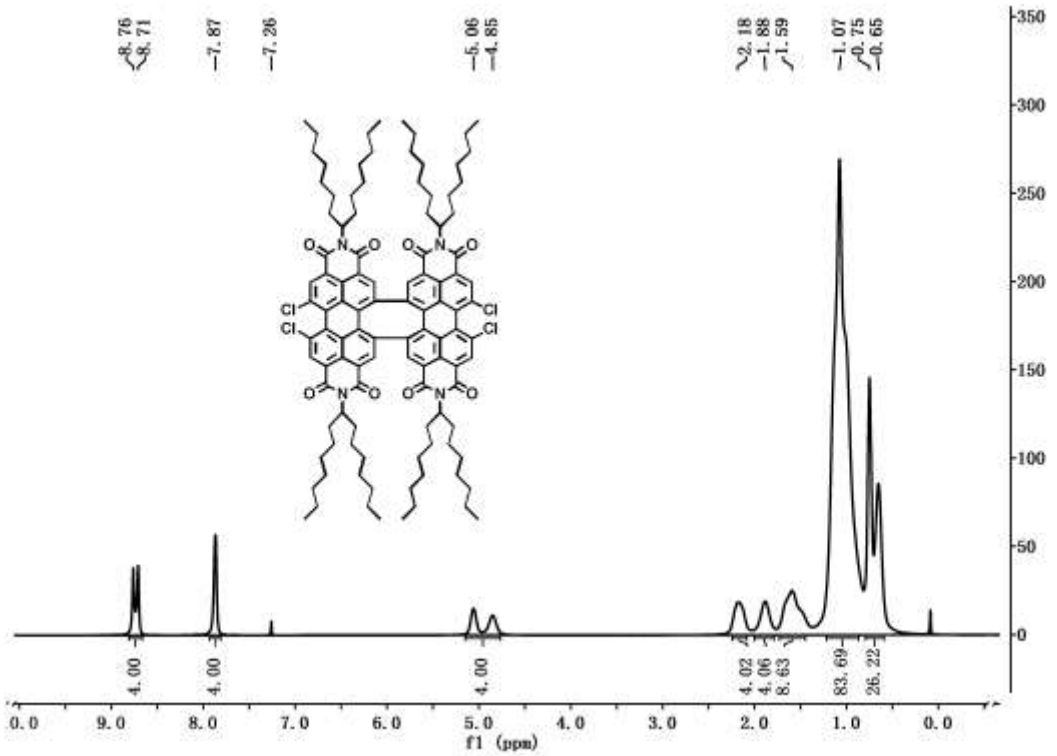
^{1}H NMR Spectrum of 2b at 400 MHz



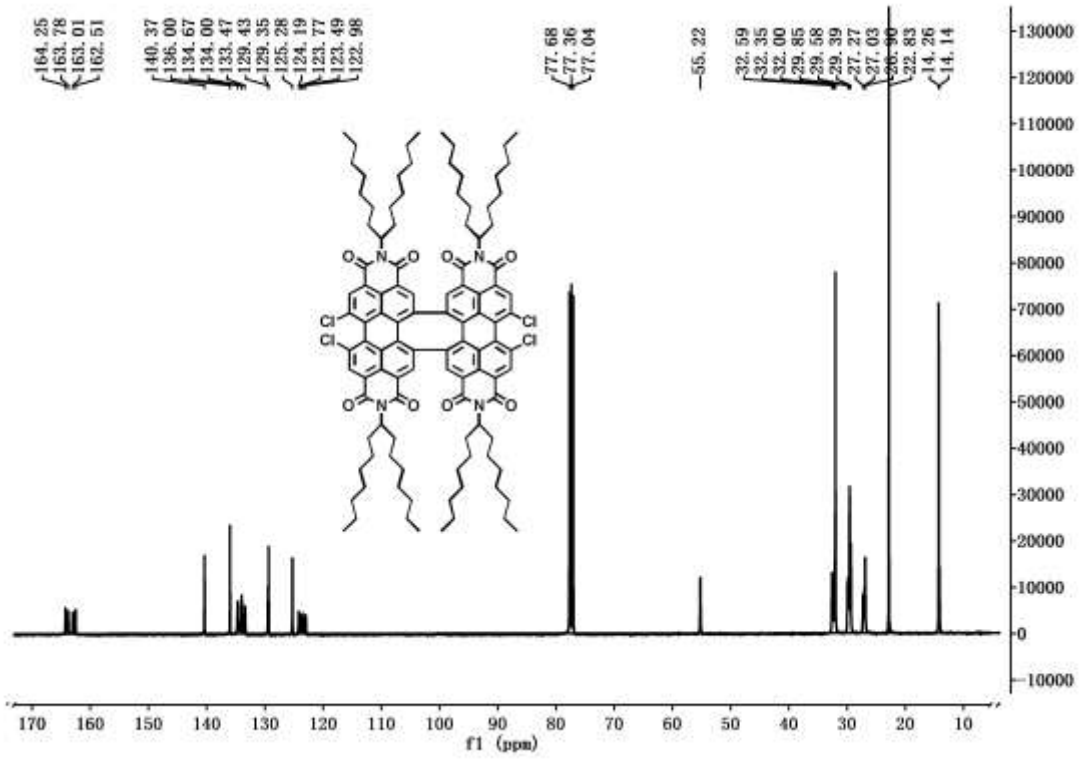
^{13}C NMR Spectrum of 2b at 100 MHz



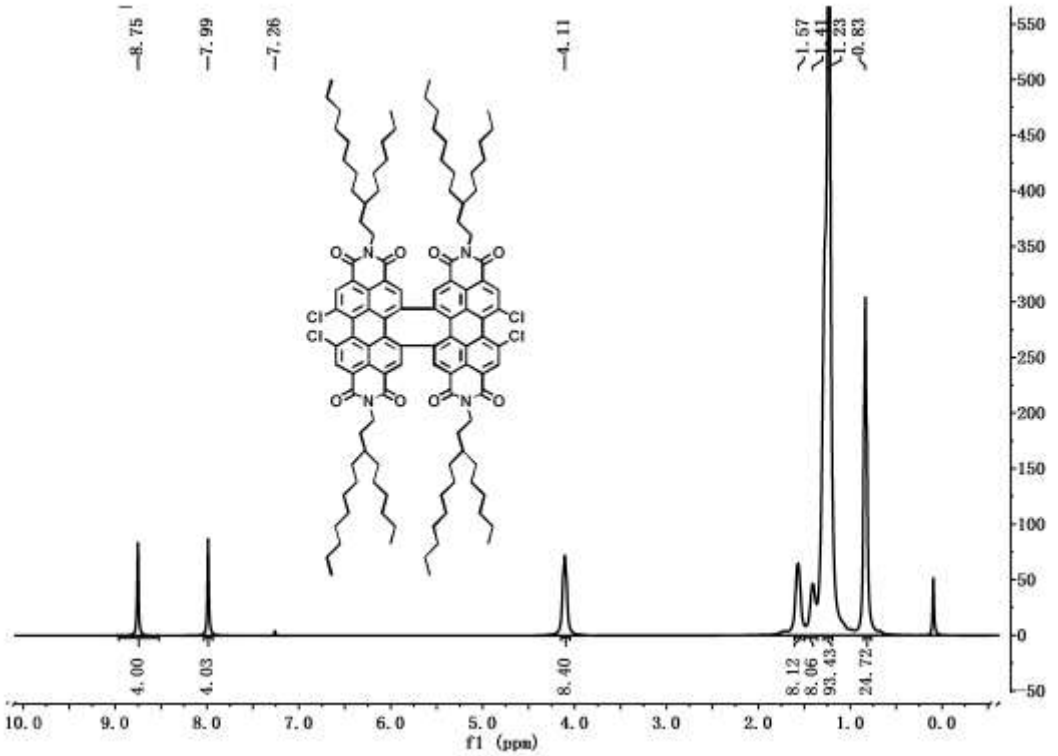
^{1}H NMR Spectrum of 2c at 400 MHz



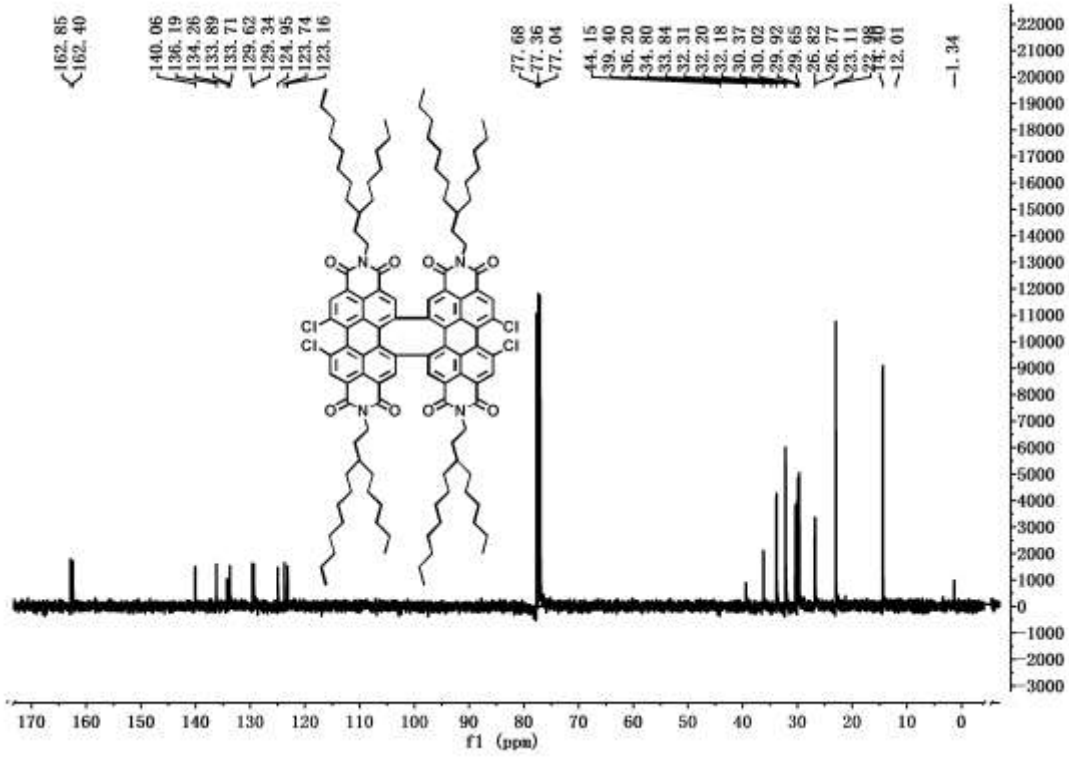
^{13}C NMR Spectrum of 2c at 100 MHz



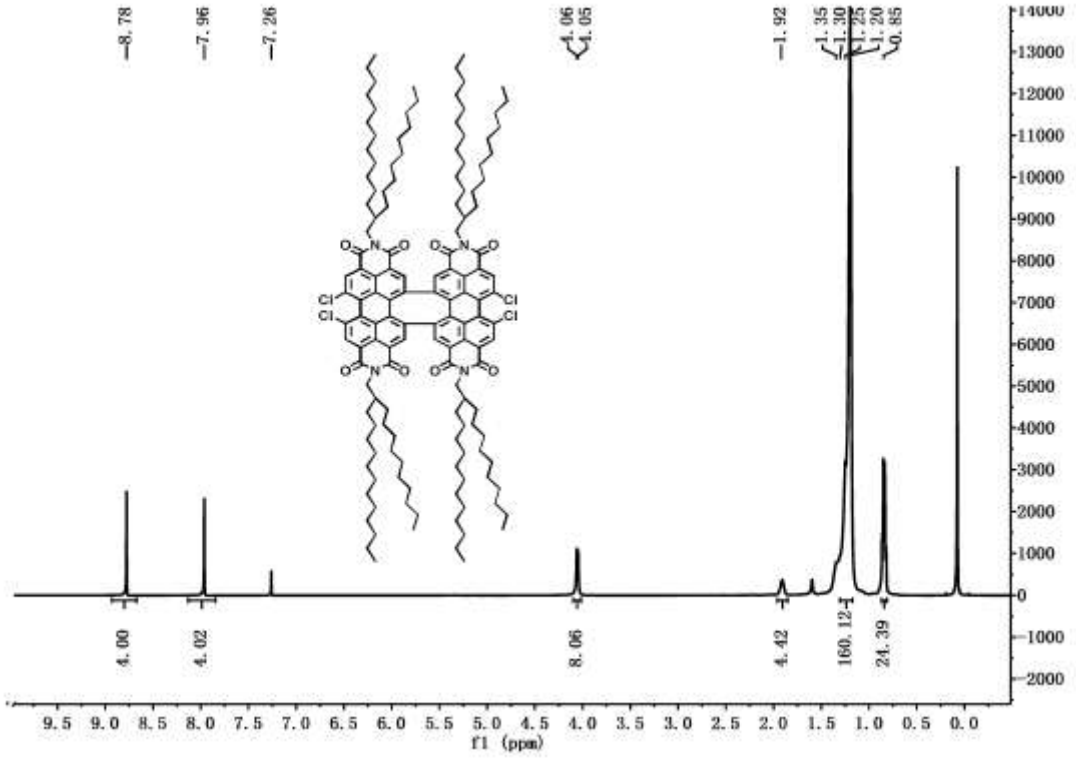
^{1}H NMR Spectrum of 2d at 400 MHz



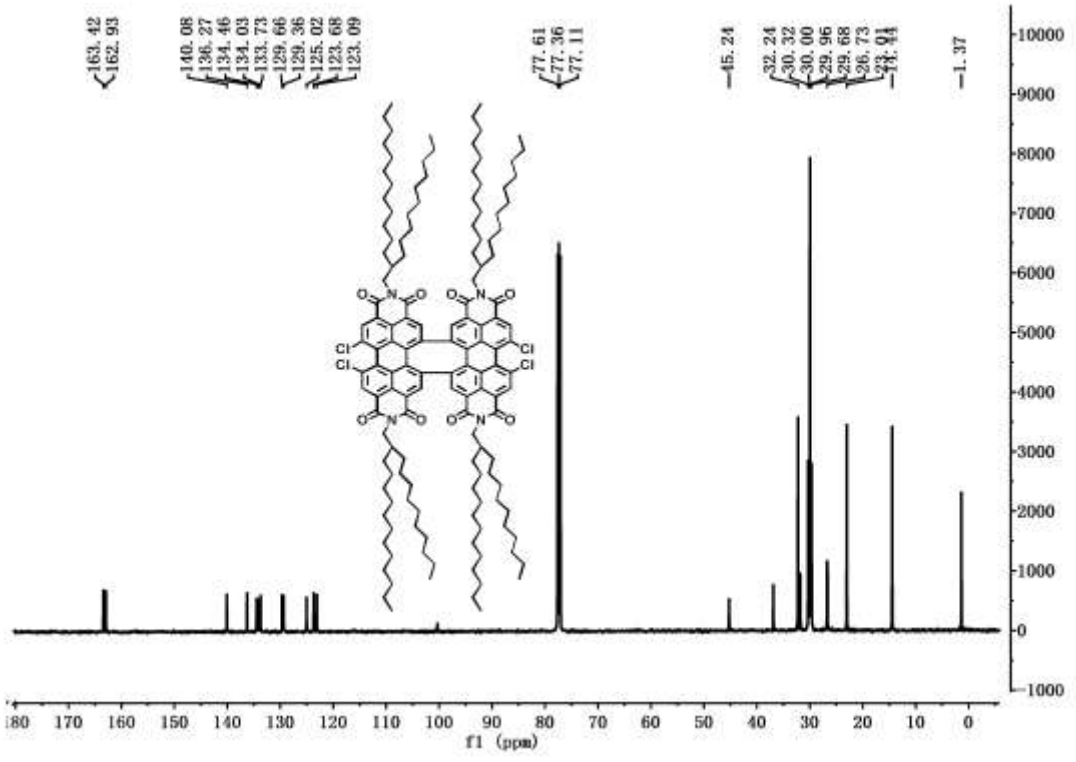
^{13}C NMR Spectrum of 2d at 100 MHz



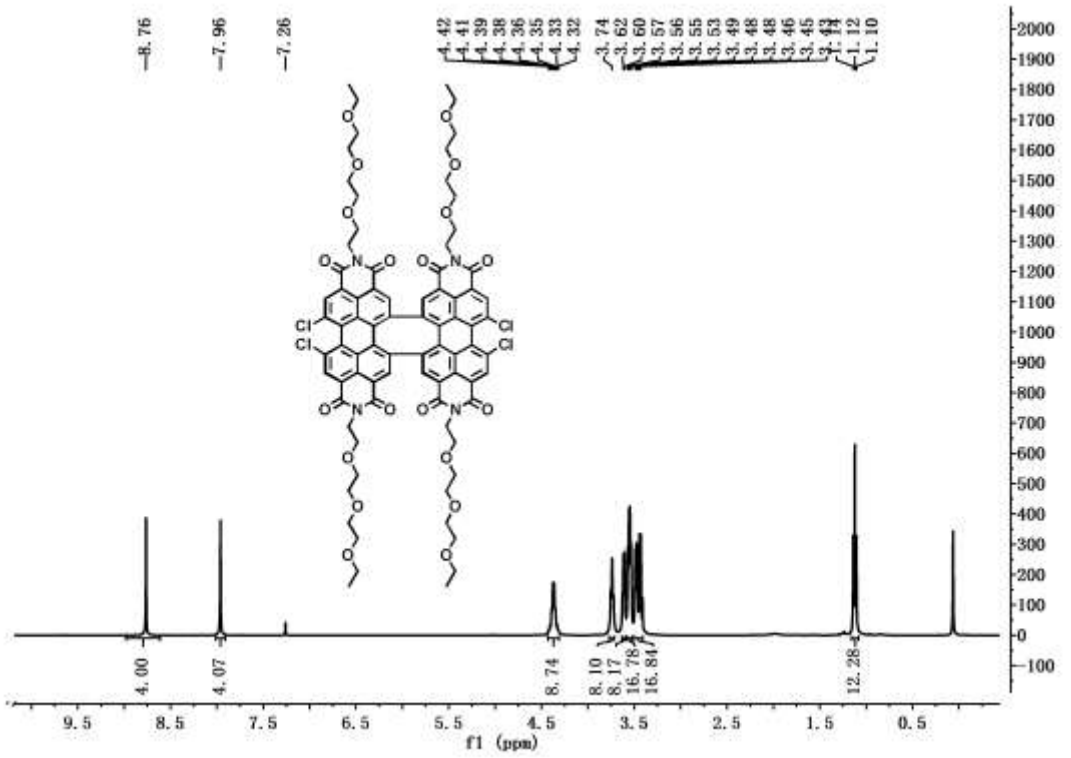
^{1}H NMR Spectrum of 2e at 400 MHz



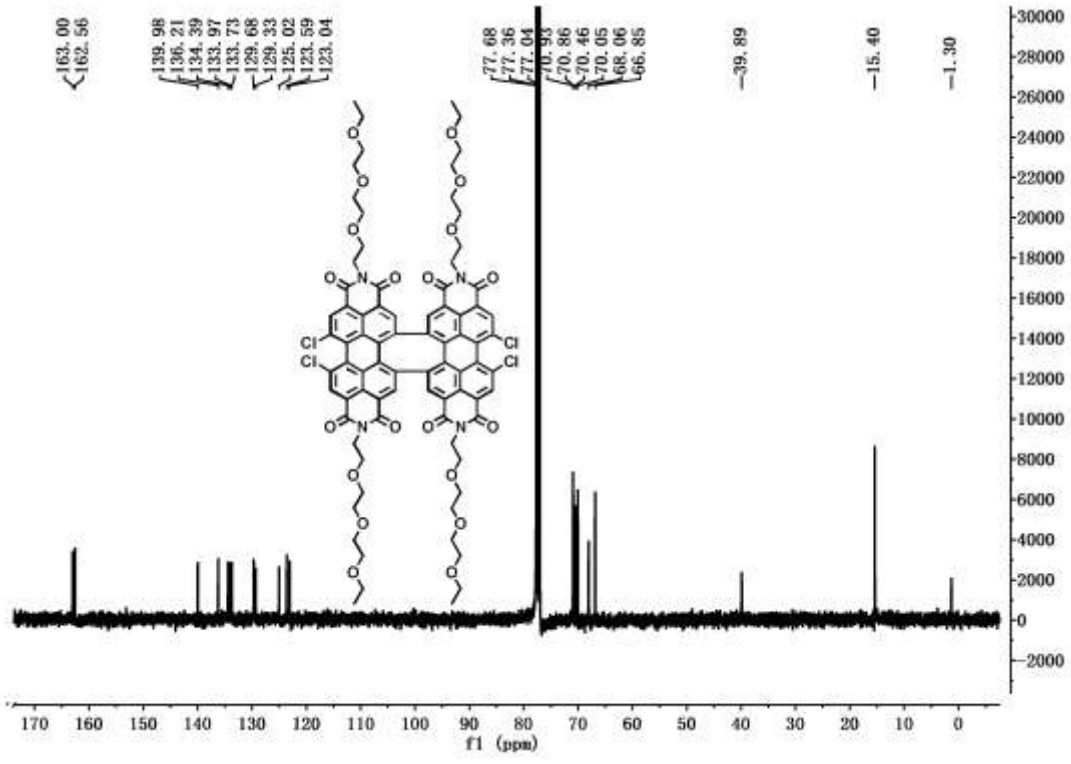
^{13}C NMR Spectrum of 2e at 100 MHz



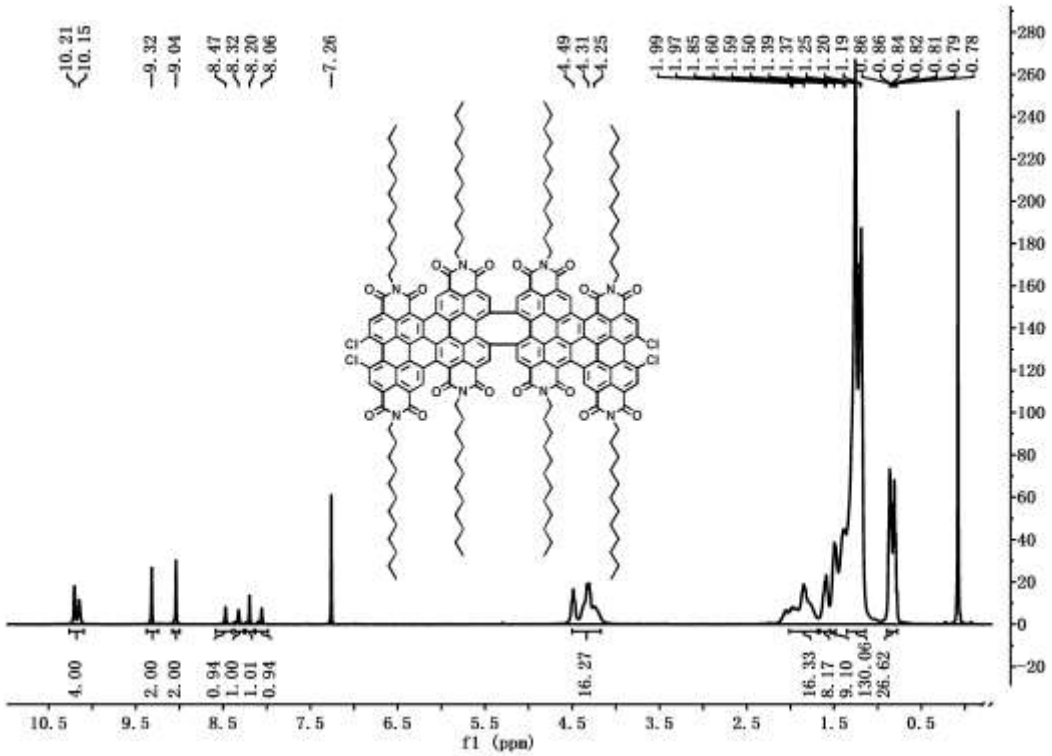
^{1}H NMR Spectrum of 2f at 400 MHz



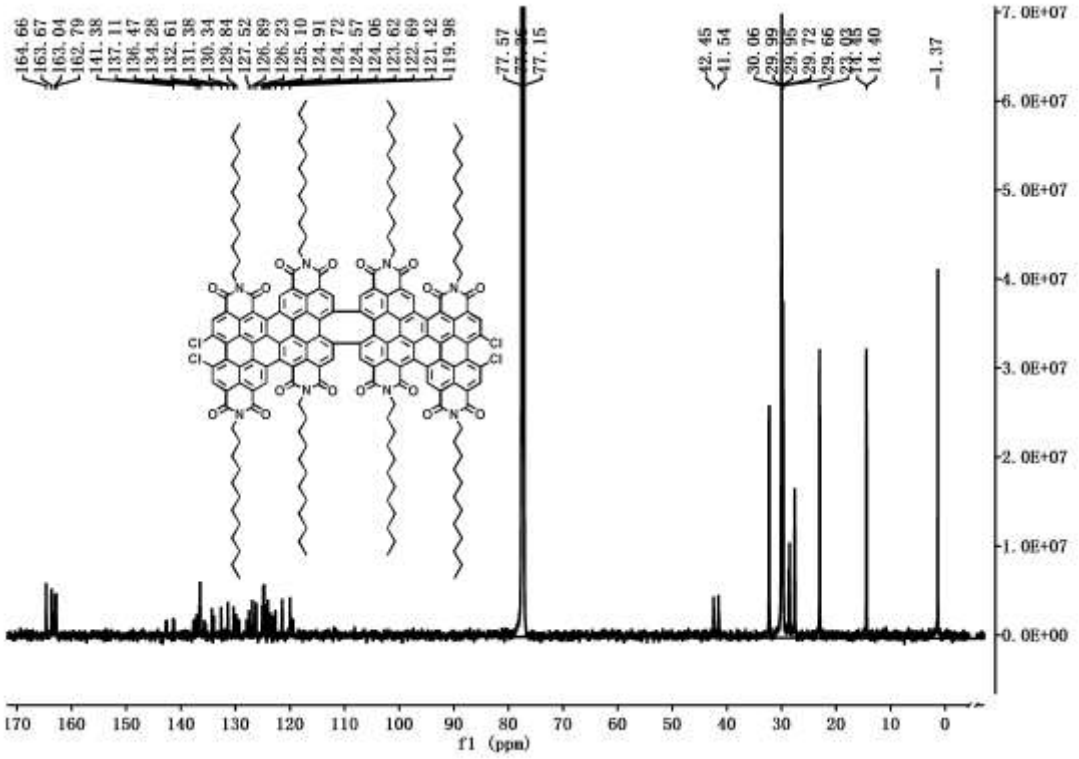
^{13}C NMR Spectrum of 2f at 100 MHz



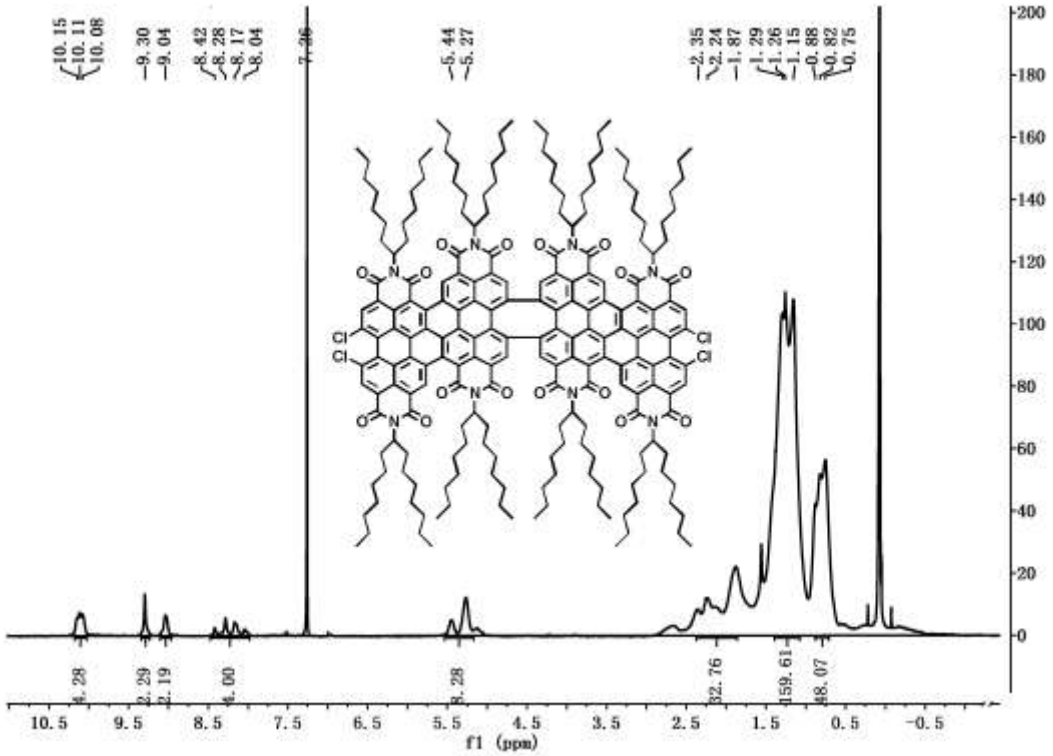
^{1}H NMR Spectrum of 4a at 600 MHz



^{13}C NMR Spectrum of 4a at 150 MHz



^{1}H NMR Spectrum of 4b at 600 MHz



^{13}C NMR Spectrum of 4b at 150 MHz