Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supplementary Information:

Subnaphthalocyanine Triimides: Potential Three-Dimensional Solution Processable Acceptors for Organic Solar Cells

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‡Author contributions. C. Cai, S. Chen and L. Li contributed equally to this work.

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1. Materials and instruments

General information

All the chemicals and solvents were obtained from commercial sources. Five donors were synthesized with reported methods.[1-5]

Measurements and characterization

^{1}H NMR and ^{13}C NMR spectra were measured on a NMR spectrometer with $CDCl_3$ as the solvent. UV-vis absorption spectra were recorded on a PerkinElmer lambda 750 Spectrophotometer. Fluorescence spectra were measured by photoluminescence spectroscopy (Hitachi F-7000). Cyclic voltammetry (CV) was performed with an electrochemical analyzer with a three-electrode system. Working electrode: glassy carbon; reference electrode: Ag/AgCl; auxiliary electrode: Pt wire; electrolyte: tetrabutylammonium hexafluoro-phosphate (Bu_4NPF_6); internal standard: ferrocene (Fc), and were calculated using the approximation: $E_{LUMO} = -4.8 - E^1_{1/2,red}$ (*vs.* Fc/Fc^+) (eV). HOMO energy values were obtained from LUMO values and optical band gap E_g^{opt} values. Thermogravimetric analysis (TGA) measurements were performed using a Perkin–Elmer TGA–7 thermogravimetric analyzer with a heating rate of 10 °C min^{-1}.

Mobility measurements

The hole mobility was measured by hole-only devices with structure of ITO/PEDOT:PSS/PTQ10:SubNcTIs/ MoO_3/Ag. Electronic mobility was measured by electron-only device with structure of ITO/ZnO/pure SubNcTIs or PTQ10:SubNcTIs/Al. The hole and electron mobilities were calculated by MOTT–Gurney equation:

$$J = \frac{9}{8}\varepsilon_r\varepsilon_0\mu\frac{V^2}{L^3}$$

Where *J* is the current density, *L* is the film thickness of active layer, ε_0 is the permittivity of free space (8.85 x 10^{-12} F m^{-1}), ε_r is the relative dielectric constant of transport medium, μ is the charge mobility, V is the internal voltage in the device.[6] The thickness of the pure or blend film for SCLC measurement was about 90 nm.

GIWAXS measurement

The GIWAXS sample stage was equipped with a 7-axis motorized stage for the fine alignment of the sample, and the incidence angle of X-ray beam was set to be 0.11° ~ 0.13° for the neat and blend films. GIWAXS patterns were recorded with a 2D CCD detector (Rayonix SX165) and X-ray irradiation time within 100 s, dependent on the saturation level of the detector. Diffraction angles were calibrated using a sucrose standard (Monoclinic, P21, a = 10.8631 Å, b = 8.7044 Å, c = 7.7624 Å, β = 102.938°) and the sample-to-detector distance was ~ 231 mm.[7]

AFM and TEM characterizations

The specimen for AFM measurements was prepared using the same procedures as OSCs device, without MoO_3/Ag on top of the active layer. The TEM images were obtained on a JEOL-2100F transmission electron microscope and an internal charge-coupled device (CCD) camera. The active layer films for the TEM measurements were spin-coated onto ITO/PEDOT:PSS substrates, then floating the film on deionized water surface, and transferring to TEM grids.

Device fabrication and characterizations

Organic photovoltaic (OPV) devices were fabricated with an inverted structure of ITO (indium tin oxide)/ZnO/donor:acceptor/MoO_3/Ag. The conductive ITO substrates were sequentially cleaned with ultrasonication in detergent water, water, acetone, and isopropanol. After drying the ITO substrates and treating the surface with UV ozone for 20 min. The ZnO precursor solution was spun-coated at 4000 r.p.m. for 50 s onto the ITO surface. After being baked at 200 °C for 60 min in air, the substrates were transferred into a nitrogen-filled glove box. The optimized solution of active layers (1:1 weight ratio, 20 mg/mL in total weight concentration) in chlorobenzene were spun-coated at 2000 rpm, resulting in optimized active layers with thickness about 90 nm. MoO_3 (7 nm) and Ag (90 nm) were deposited by thermal evaporation under a vacuum chamber to complete the device fabrication. The effective area of one cell was 0.04 cm^2. The current-voltage (J-V) characteristics were measured by a Keithley 2400 Source Meter under simulated solar light (100 mW cm^2, AM 1.5 G, Abet Solar Simulator Sun 2000). The external quantum efficiency (EQE) spectra were detected on an IPCE measuring system (Oriel Cornerstone monochromator equipped with Oriel 70613NS QTH lamp). All the measurement was performed at room temperature under nitrogen atmosphere.

Recombination dynamics and charge separation

The photocurrent (J_{ph}) versus light intensity (P_{light}) were used to quantify the charge recombination dynamics. The correlation between J_{sc} and P_{light} was expressed as a power-law equation of $J_{sc} \propto P_{light}^{\alpha}$. If all free charge carriers are swept out and collected at the electrodes prior to recombination, α is supposed to be 1, while $\alpha < 1$, bimolecular recombination exists.[8]

To investigate the charge generation and dissociation process of these acceptors, the photo-generated current density ($J_{ph} = J_L - J_D$, J_L: current density under illumination; J_D: current density in the dark) versus the effective voltage ($V_{eff} = V_0 - V_a$, V_0: the voltage when the J_{ph} is zero; V_a: applied voltage) of the BHJOSCs were measured. At high V_{eff} (> 2 V), all the photogenerated excitons were dissociated into free charge carriers and collected by electrodes, and the saturation photocurrent density (J_{sat}) was only limited by the absorbed incident photons. Therefore, the P_{diss}, which is determined by normalizing J_{sc} with J_{sat} ($P_{diss} = J_{sc}/J_{sat}$) was also calculated to evaluate the exciton dissociation and charge recombination.[9]

2. Structure of $PC_{61}BM$, $PC_{71}BM$, ITIC, IT-4F, FTTB-PDI_4, and N2200

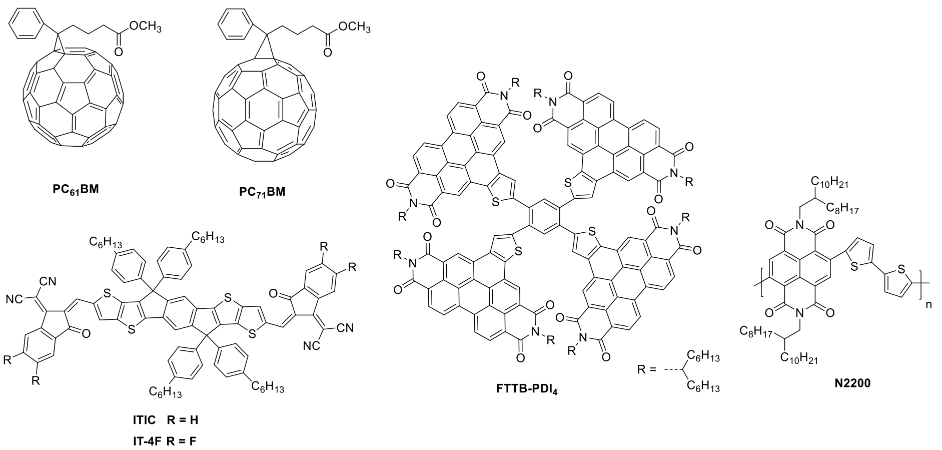


Fig. S1. Structure of $PC_{61}BM$, $PC_{71}BM$, ITIC, IT-4F, FTTB-PDI_4, and N2200.

3. Structure of SubPc and SubNc-Cl

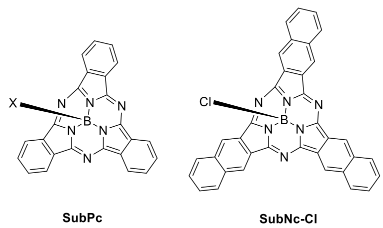
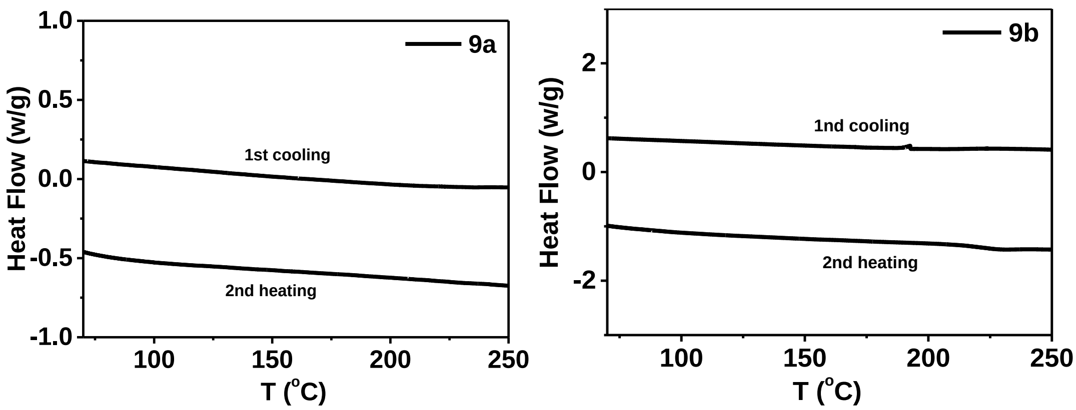


Fig. S2. Structure of SubPc and SubNc-Cl.

4. DSC curves



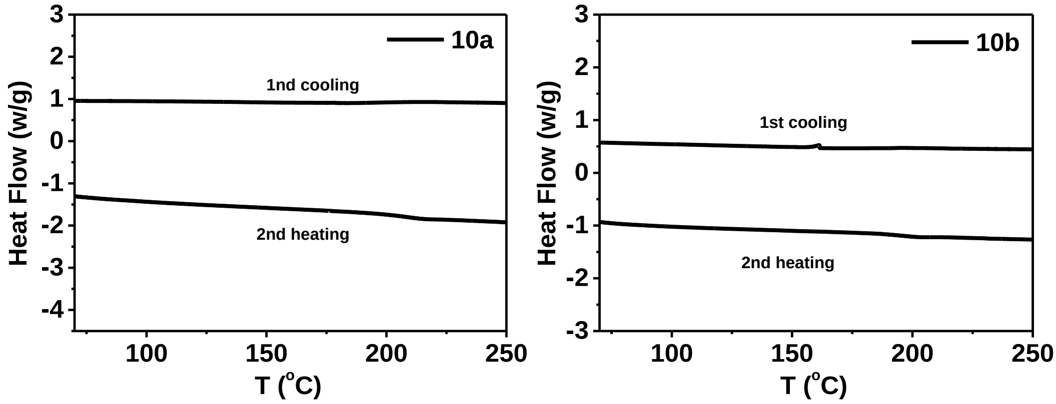


Fig. S3. DSC curves of SubNcTIs, heating and cooling rate is 10 °C/min.

5. Fluorescence spectra

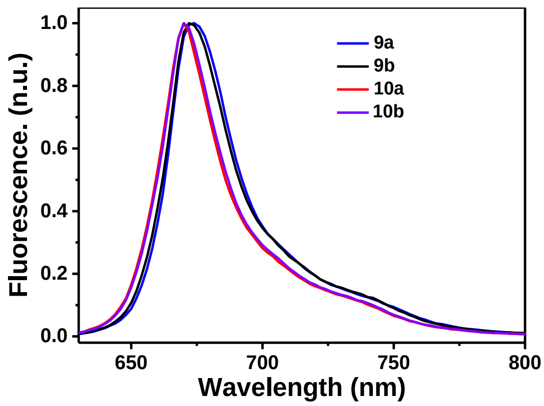
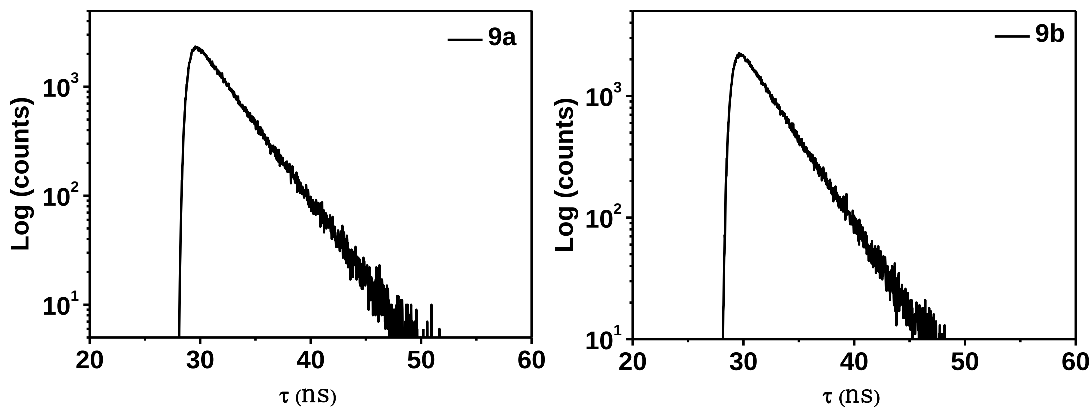


Fig. S4. Fluorescence spectra of SubNcTIs in $CHCl_3$ at 10^{-6} mol L^{-1} (λ_{ex} = 620 nm).

6. Fluorescence decayed curves



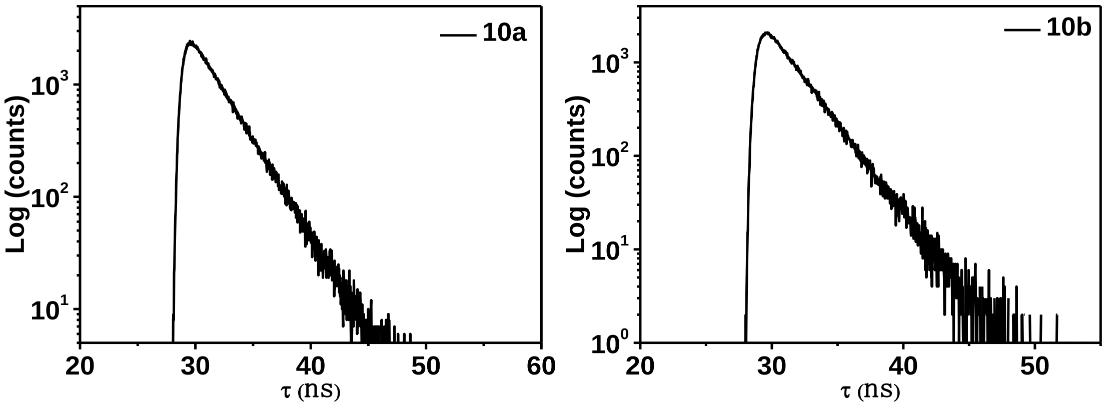


Fig. S5. Fluorescence decayed curves of SubNcTIs in $CHCl_3$ solution.

7. Cyclic voltammograms

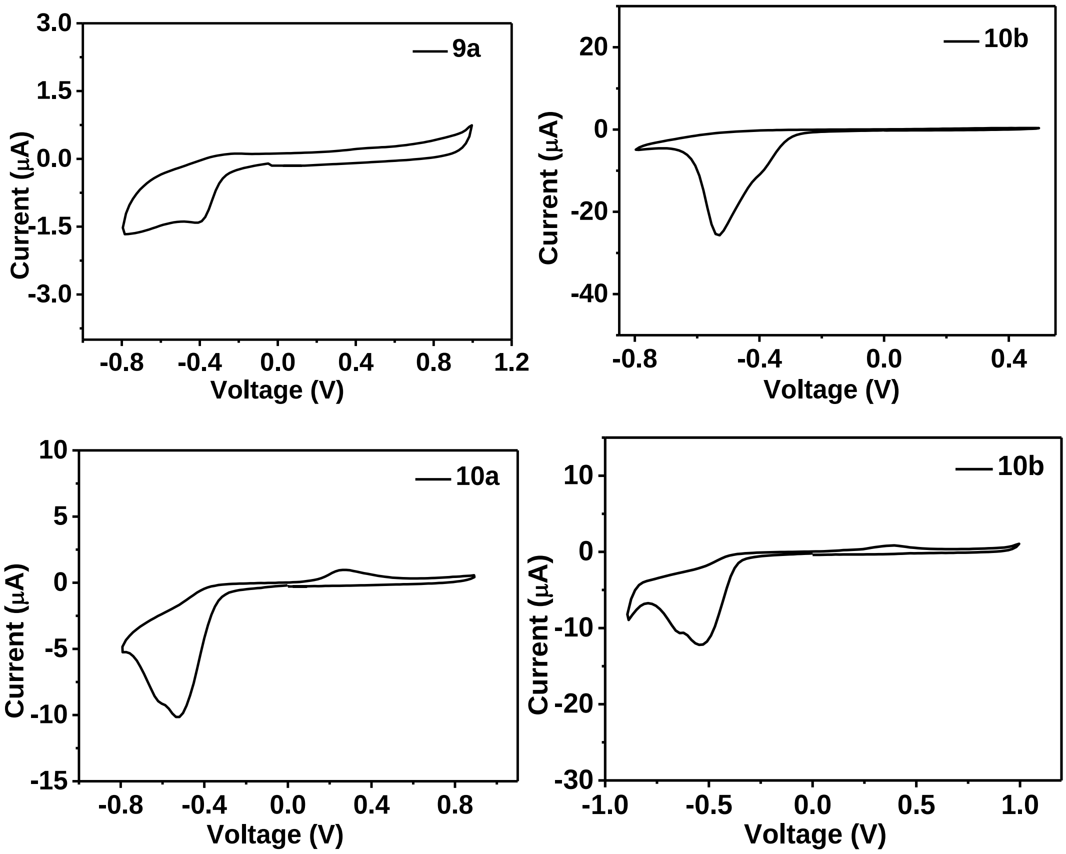
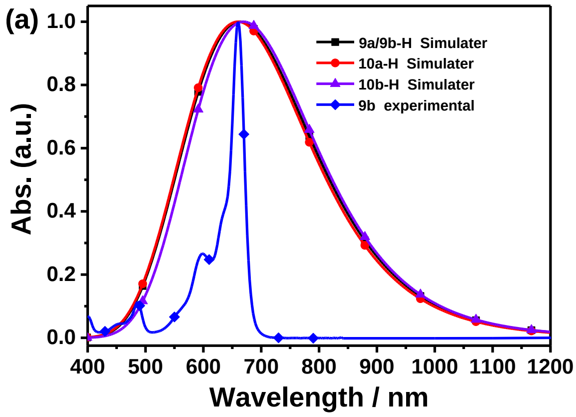


Fig. S6. Cyclic voltammograms of SubNcTIs.

8. Simulated molecular absorption, geometries, and band gaps



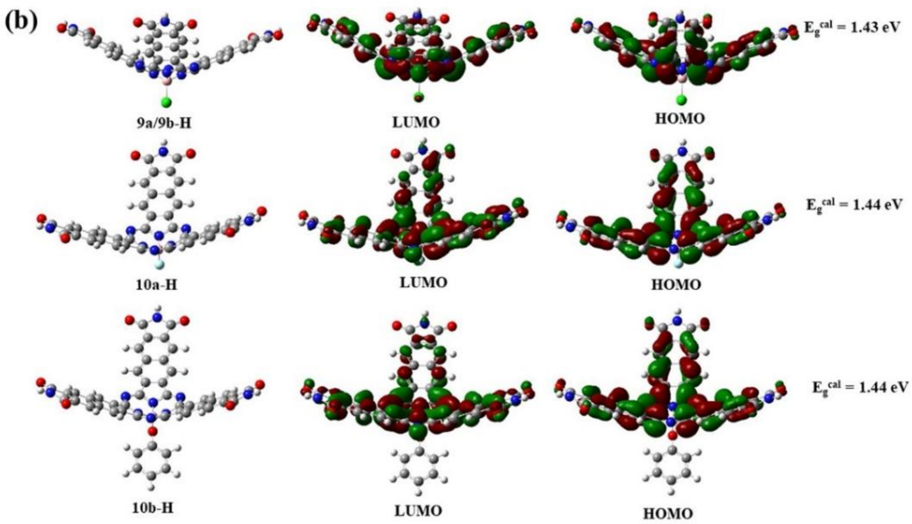
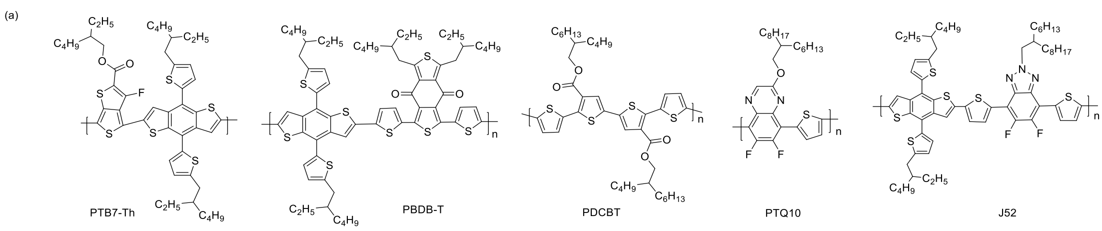


Fig. S7. Simulated molecular absorption (a), geometries, and band gaps (b) of SubNcTIs.

9. Structure, absorption, and energy levels of donors and 9b



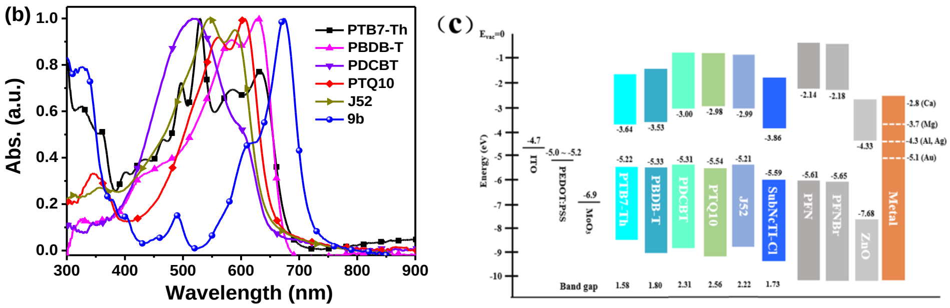


Fig. S8. (a) Structure of five donors, (b) absorption of donors and **9b** in film, and (c) energy levels of donors and **9b**.

10. Optimization of fabricating conditions of solar cells

Table S1. Photovoltaic properties of OSCs based on 9b with different donors at the ratio of 10:10 mg/mL.

Donors	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
PTB7-Th	0.89	6.59	36.68	2.14
PBDT-T	0.90	5.96	41.24	2.21
PDCBT	0.88	6.27	35.09	1.93
PTQ10	1.11	9.50	42.73	4.51
J52	0.84	9.68	45.50	3.71

All devices were measured under the illumination of AM 1.5G, 100 mW cm^{-2}.

Table S2. Photovoltaic properties of OSCs based on PTQ10:9b with different D:A ratios.

D/A [w/w]	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
15:10	1.11	7.28	45.19	3.65
12:10	1.11	8.29	42.73	3.94
10:10	1.11	9.50	42.73	4.51
10:12	1.10	8.72	42.80	4.13
10:15	1.10	8.29	38.85	3.55

All devices were measured under the illumination of AM 1.5G, 100 mW cm^{-2}.

Table S3. Photovoltaic properties of OSCs based on PTQ10:9b (D:A=1:1) with different additives.

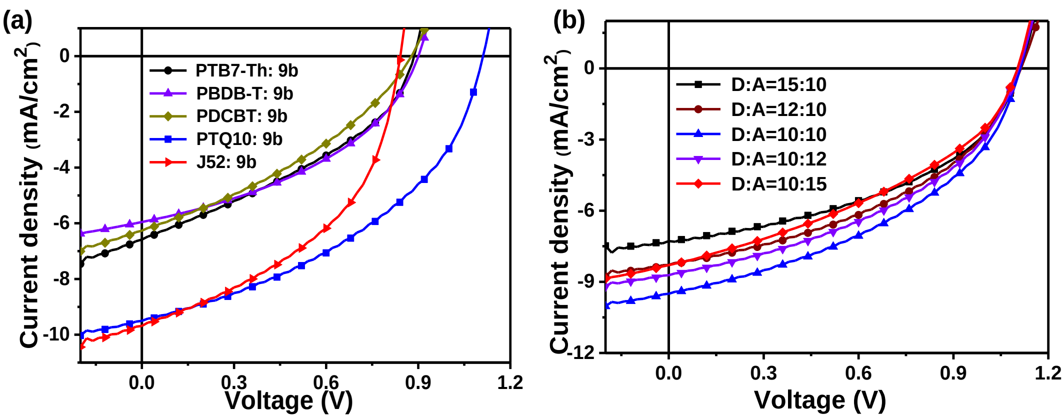
Additives	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
w/o	1.11	9.50	42.73	4.51
1% DIO	1.10	10.43	45.49	5.20
1% CN	1.10	7.91	47.12	4.12
1% NMP	1.10	8.61	44.69	4.25
1% DPE	1.10	8.68	48.75	4.67

All devices were measured under the illumination of AM 1.5G, 100 mW cm^{-2}.

Table S4. Photovoltaic properties of OSCs based on PTQ10:9b (D:A=1:1) with different additives (DIO and DPE) ratios.

Additives	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
0.25% DIO + 0.25% DPE	1.09	11.79	43.35	5.60
0.5% DIO + 0.5% DPE	1.08	13.98	41.34	6.25
0.75% DIO + 0.5% DPE	1.10	11.89	44.67	5.84
0.75% DIO + 0.75% DPE	1.10	10.77	45.03	5.34
1% DIO + 1% DPE	1.09	10.54	44.25	5.40

All devices were measured under the illumination of AM 1.5G, 100 mW cm^{-2}.



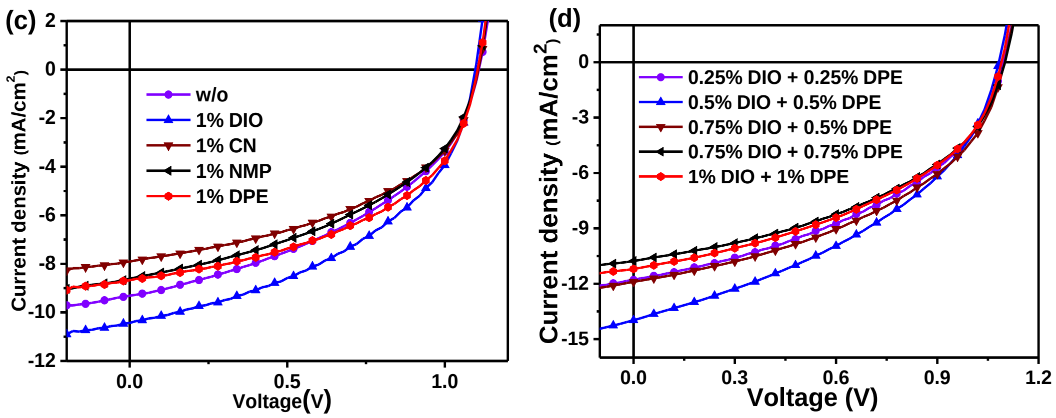


Fig. S9. (a) Photovoltaic properties of OSCs based on **9b** with different donors at the ratio of 10:10 mg/mL, (b) photovoltaic properties of OSCs based on PTQ10:**9a** with different D:A ratios, (c) photovoltaic properties of OSCs based on PTQ10:**9a** (D:A=1:1) with different additives, and (d) photovoltaic properties of OSCs based on PTQ10:**9a** (D:A=1:1) with different ratios of DIO and DPE.

11. *J-V* Curves for carrier mobility

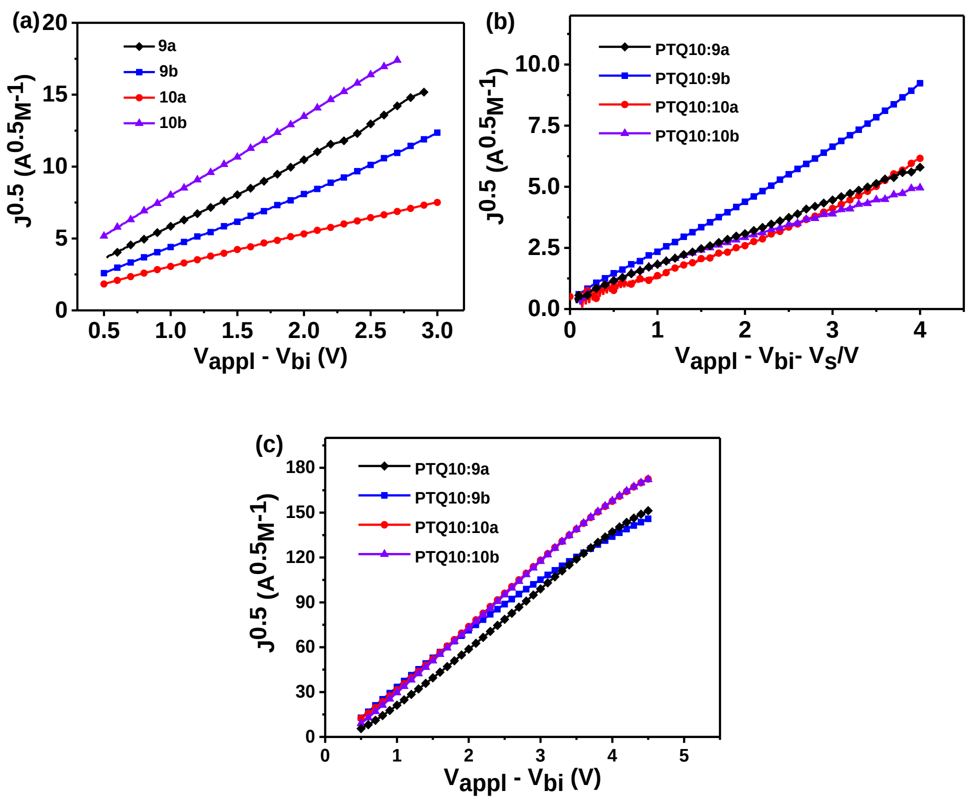


Fig. S10. (a) Current density–voltage and SCLC fitting curves of SubNcTIs neat films only electron devices, (b) blend films only electron devices, and (c) blend films only hole devices.

12. TEM images of blend films for optimized devices

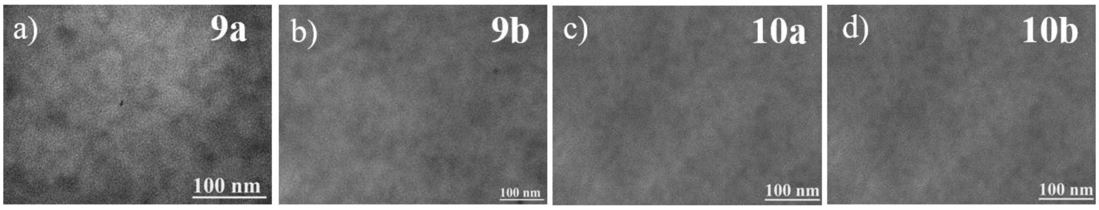


Fig. S11. TEM images of blend films for optimized devices.

13. DFT cartesian coordinates, total energy, and imaginary frequencies

Table S5. Cartesian coordinates, total energies and imaginary frequencies of the DFT optimized geometry of SubNcTIs.

9a/9b-H:
Calculation Type = FREQ
Calculation Method = RPBEPBE
Basis Set = 6-311G(d,p)
Charge = 0
Spin = Singlet
E(RPBE-PBE) = -3036.47654206 a.u.
RMS Gradient Norm = 0.00000074 a.u.
Imaginary Freq = 0
Dipole Moment = 0.7065 Debye
Point Group = C1

Coordinates
0 1

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2	C	-3.288255	-0.725923	0.945583
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4	C	-5.482117	-0.729457	-0.07314
5	C	-5.482327	0.727893	-0.073136
6	C	-4.359701	1.432796	0.430127
7	C	-6.614661	-1.43343	-0.584948
8	C	-7.679255	-0.711436	-1.065136
9	C	-7.67946	0.709246	-1.065132
10	C	-6.615074	1.431543	-0.58494
11	C	-8.971429	-1.185074	-1.648531
12	C	-8.971773	1.182512	-1.648524
13	O	-9.370541	2.317908	-1.828602
14	O	-9.369867	-2.320585	-1.828618
15	C	2.269042	2.481424	0.972972
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17	C	0.938063	4.486348	0.441775
18	C	2.111952	5.102679	-0.060873
19	C	3.373899	4.373604	-0.050837
20	C	3.42054	3.052259	0.460847
21	C	2.070541	6.430785	-0.585062
22	C	3.229424	6.986204	-1.068528
23	C	4.459667	6.275536	-1.058246
24	C	4.551432	4.997518	-0.564861
25	C	3.467193	8.335361	-1.666715
26	C	5.517257	7.151273	-1.649074
27	O	6.700095	6.926356	-1.824746
28	O	2.683654	9.246105	-1.859457
29	C	1.013564	-3.206619	0.963587
30	C	2.269752	-2.480777	0.972967

31	C	3.421416	-3.051282	0.460852
32	C	3.375156	-4.372638	-0.050837
33	C	2.113414	-5.102071	-0.060892
34	C	0.939346	-4.486074	0.441749
35	C	4.552871	-4.996219	-0.564845
36	C	4.461473	-6.27426	-1.058237
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38	C	2.072383	-6.430185	-0.585089
39	C	5.519318	-7.149702	-1.649048
40	C	3.469587	-8.334364	-1.666723
41	O	2.686305	-9.245329	-1.85948
42	O	6.702096	-6.924452	-1.824703
43	C	-0.007758	-2.301671	1.479272
44	N	0.677429	-1.185559	1.900791
45	C	1.990651	-1.147355	1.493465
46	C	-1.996246	1.15374	1.468877
47	N	-1.37521	-0.000198	1.887367
48	C	-1.995915	-1.15431	1.468873
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50	N	0.677092	1.185747	1.900793
51	C	-0.008415	2.301669	1.479284
52	N	2.679289	0.000381	1.365053
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54	B	-0.010676	-0.000004	2.501765
55	N	-1.344953	-2.323565	1.338382
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60	H	-6.628689	2.524428	-0.590818
61	H	-0.013274	5.022581	0.416965
62	H	4.360377	2.495724	0.449982
63	H	1.130882	6.988866	-0.598231
64	H	5.504371	4.462241	-0.563194
65	H	4.361096	-2.494482	0.449997
66	H	-0.01184	-5.022576	0.416929
67	H	5.505659	-4.460674	-0.563164
68	H	1.132881	-6.98853	-0.598274
69	N	4.843957	-8.341951	-1.977788
70	H	5.30902	-9.140215	-2.404412
71	N	-9.668477	-0.001381	-1.963017
72	H	-10.59641	-0.001515	-2.380682
73	N	4.841554	8.343329	-1.977812
74	H	5.306387	9.141726	-2.40444

10a-H:
Calculation Type = FREQ
Calculation Method = RPBEPBE
Basis Set = 6-311G(d,p)
Charge = 0
Spin = Singlet
E(RPBE-PBE) = -2676.24623248 a.u.
RMS Gradient Norm = 0.00000889 a.u.
Imaginary Freq = 0
Dipole Moment = 0.3186 Debye
Point Group = C1

Coordinates

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51	C	2.077614	0.989851	1.596997
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53	N	1.521001	2.206496	1.460637
54	B	0.002659	-0.00044	2.644417
55	N	-2.671407	0.212971	1.468849
56	F	0.004975	0.000034	4.038399
57	H	-4.144663	2.83344	0.536982
58	H	0.417041	5.00172	0.531757
59	H	-5.120256	4.884086	-0.487902
60	H	-0.558774	7.052387	-0.492205
61	H	4.527058	2.17147	0.528017
62	H	4.124095	-2.86328	0.527073
63	H	6.792996	1.990166	-0.49139
64	H	6.389688	-3.044337	-0.492762
65	H	-0.382628	-5.003324	0.525108
66	H	-4.543811	-2.140601	0.543233
67	H	-1.672287	-6.870922	-0.502212
68	H	-5.834317	-4.009782	-0.479348
69	N	9.610052	-0.768913	-1.890548
70	H	10.531001	-0.842691	-2.317018
71	N	-4.138927	8.69882	-1.89792
72	H	-4.535247	9.531702	-2.327702
73	N	-5.472311	-7.929526	-1.896163
74	H	-5.996713	-8.68881	-2.325062

10b-H:
Calculation Type = FREQ
Calculation Method = RPBEPBE
Basis Set = 6-311G(d,p)
Charge = 0
Spin = Singlet
E(RPBE-PBE) = -2883.01612079 a.u.
RMS Gradient Norm = 0.00000073 a.u.
Imaginary Freq = 0
Dipole Moment = 1.5896 Debye
Point Group = C1

coordinates

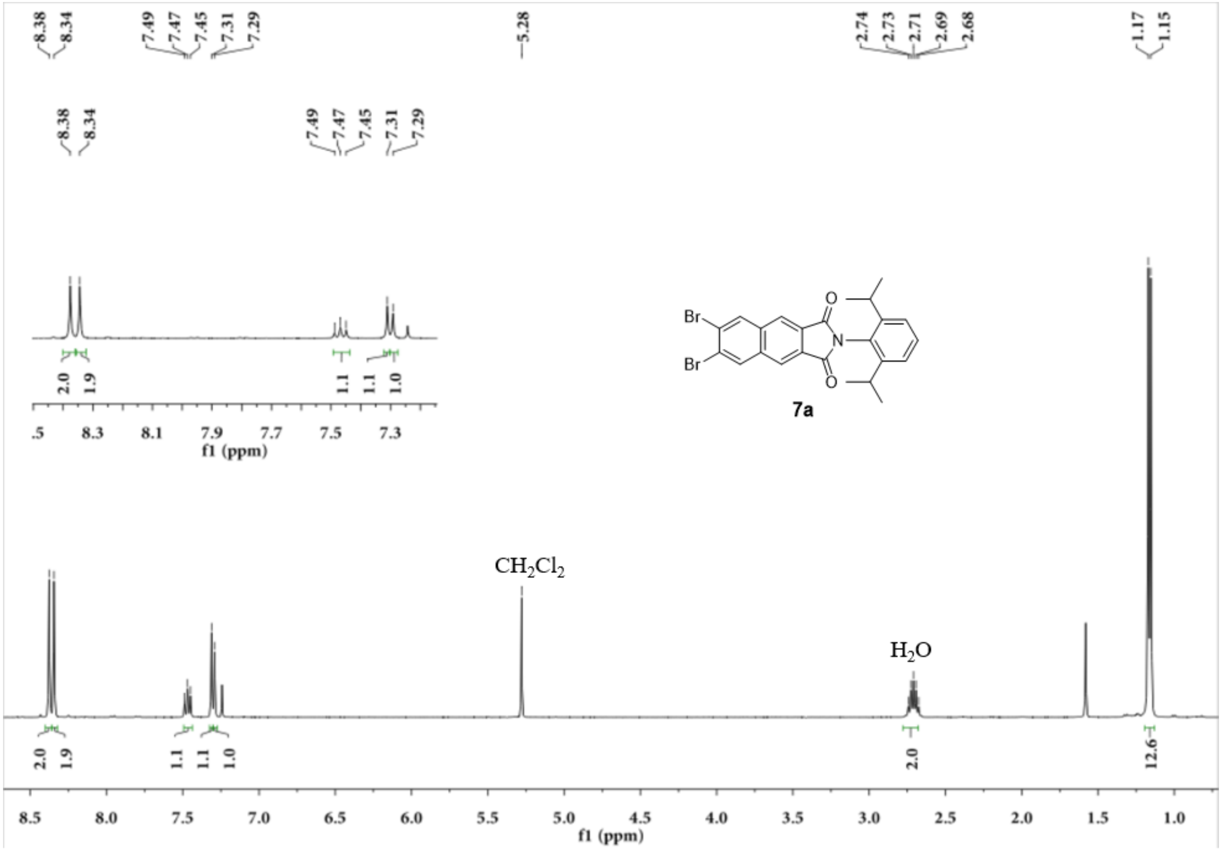
0 1

1	C	-0.978672	-3.169066	0.468787
2	C	-2.200821	-2.393919	0.375048
3	C	-3.327978	-2.91955	-0.230809
4	C	-3.292627	-4.243371	-0.737644
5	C	-2.064134	-5.022071	-0.644864
6	C	-0.911797	-4.451178	-0.04743
7	C	-4.448264	-4.822273	-1.345435
8	C	-4.368185	-6.105019	-1.828757
9	C	-3.1704	-6.864054	-1.738676
10	C	-2.03325	-6.352485	-1.163773
11	C	-5.408242	-6.940162	-2.502774
12	C	-3.412353	-8.204817	-2.352955
13	O	-2.653151	-9.147358	-2.480373
14	O	-6.563491	-6.669904	-2.773637
15	C	3.458033	0.586027	0.782462
16	C	3.399506	-0.863348	0.780206
17	C	4.473434	-1.614574	0.33709
18	C	5.655713	-0.956438	-0.086664
19	C	5.714722	0.499756	-0.084107
20	C	4.589232	1.249673	0.341851
21	C	6.79173	-1.705874	-0.520155
22	C	7.915476	-1.028109	-0.924044
23	C	7.972986	0.39161	-0.921811
24	C	6.907591	1.156488	-0.51538
25	C	9.224976	-1.55413	-1.415806
26	C	9.320762	0.811555	-1.412559
27	O	9.777153	1.92961	-1.563093
28	O	9.589666	-2.704958	-1.569405
29	C	-2.000772	2.561912	0.378937
30	C	-0.720323	3.235827	0.476069
31	C	-0.548772	4.508521	-0.038926
32	C	-1.649163	5.170415	-0.640145
33	C	-2.93611	4.493553	-0.73758
34	C	-3.079861	3.177011	-0.230546
35	C	-1.508878	6.493541	-1.159695
36	C	-2.598283	7.09452	-1.74056
37	C	-3.853145	6.434713	-1.835207
38	C	-4.038641	5.163402	-1.35066

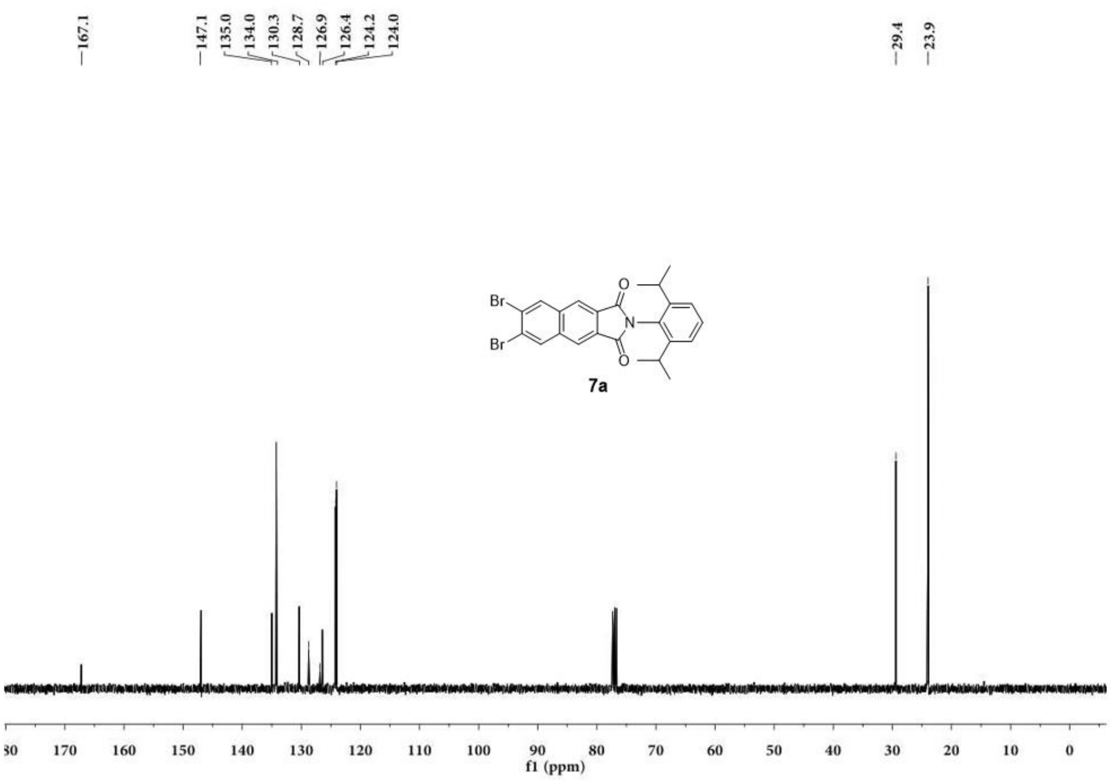
39	C	-2.728393	8.449653	-2.357212
40	C	-4.819419	7.350309	-2.514464
41	O	-5.99167	7.174291	-2.789821
42	O	-1.895145	9.327753	-2.482188
43	C	-1.818769	1.220036	0.923221
44	N	-0.547117	1.206019	1.445954
45	C	0.214579	2.291158	1.078651
46	C	0.029872	-2.303526	1.072095
47	N	-0.641825	-1.161425	1.442418
48	C	-1.910707	-1.071953	0.920775
49	C	2.150245	1.064961	1.218597
50	N	1.457745	-0.060478	1.594024
51	C	2.057502	-1.236946	1.215295
52	N	1.558574	2.259726	1.040085
53	N	1.371965	-2.379964	1.033287
54	B	0.052556	-0.004536	2.131967
55	N	-2.539182	0.101292	0.729947
56	H	-4.2408	-2.32596	-0.318213
57	H	0.016757	-5.024332	0.004241
58	H	-5.376048	-4.249461	-1.421621
59	H	-1.118131	-6.946917	-1.101479
60	H	4.419188	-2.705406	0.316916
61	H	4.622876	2.341402	0.325234
62	H	6.761324	-2.798446	-0.526846
63	H	6.965289	2.24795	-0.518491
64	H	0.42287	5.004797	0.015512
65	H	-4.03704	2.658427	-0.321155
66	H	-0.549155	7.012546	-1.093997
67	H	-5.009375	4.667346	-1.429938
68	O	0.058664	-0.005834	3.569829
69	C	-1.121215	0.045013	4.284731
70	C	-1.642009	1.283714	4.689918
71	C	-1.770747	-1.142448	4.656302
72	C	-2.813488	1.329903	5.452549
73	H	-1.110855	2.197494	4.415002
74	C	-2.942023	-1.085401	5.418663
75	H	-1.338756	-2.099788	4.356965
76	C	-3.470028	0.148405	5.816153
77	H	-3.21215	2.297081	5.768149
78	H	-3.441289	-2.013332	5.707827
79	H	-4.382684	0.188637	6.414331
80	N	-4.756036	-8.159347	-2.77532
81	H	-5.216105	-8.940264	-3.237837
82	N	9.989752	-0.399917	-1.678509
83	H	10.943717	-0.438025	-2.030514
84	N	-4.069464	8.512261	-2.785604
85	H	-4.462857	9.32718	-3.250974

14. ^{1}H and ^{13}C NMR spectra

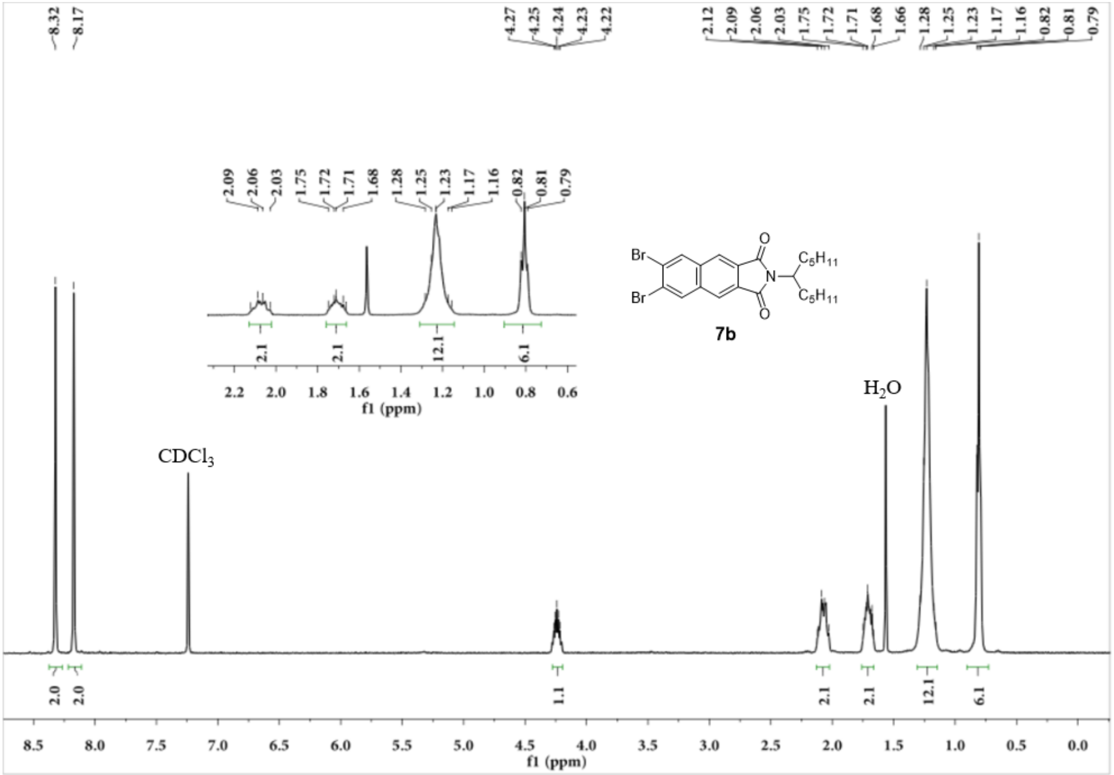
^{1}H NMR of compound **7a** in $CDCl_3$ (400 MHz)



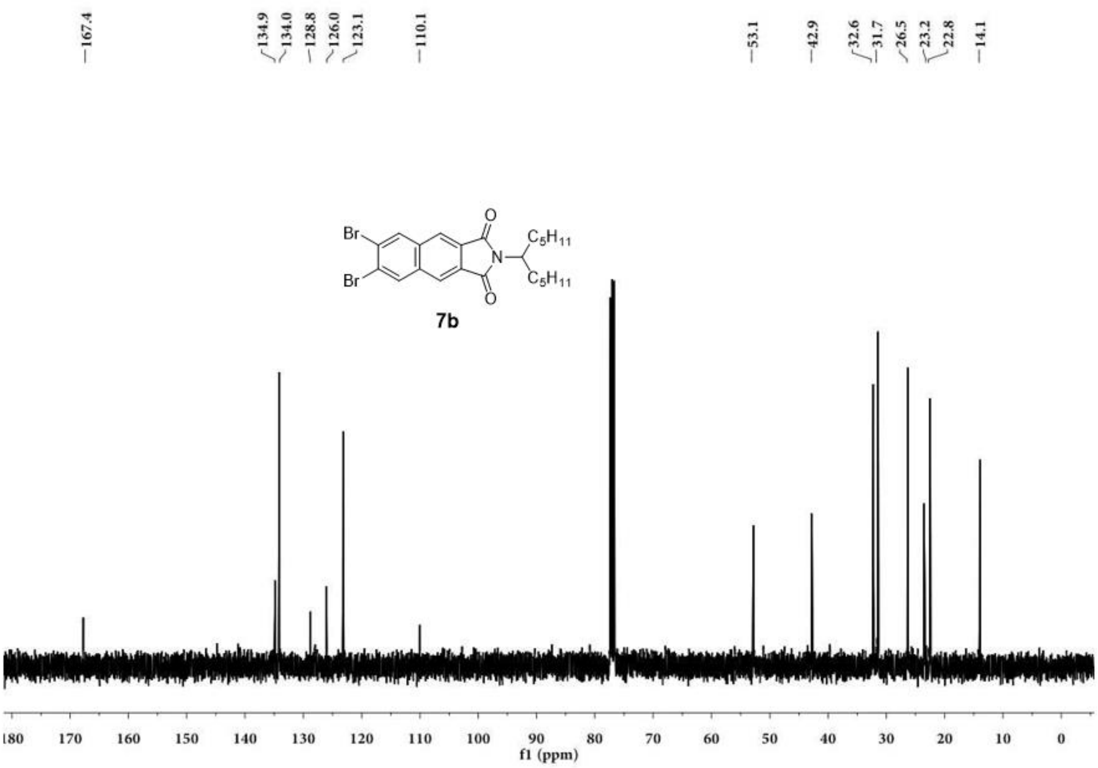
^{13}C NMR of compound **7a** in $CDCl_3$ (101 MHz)



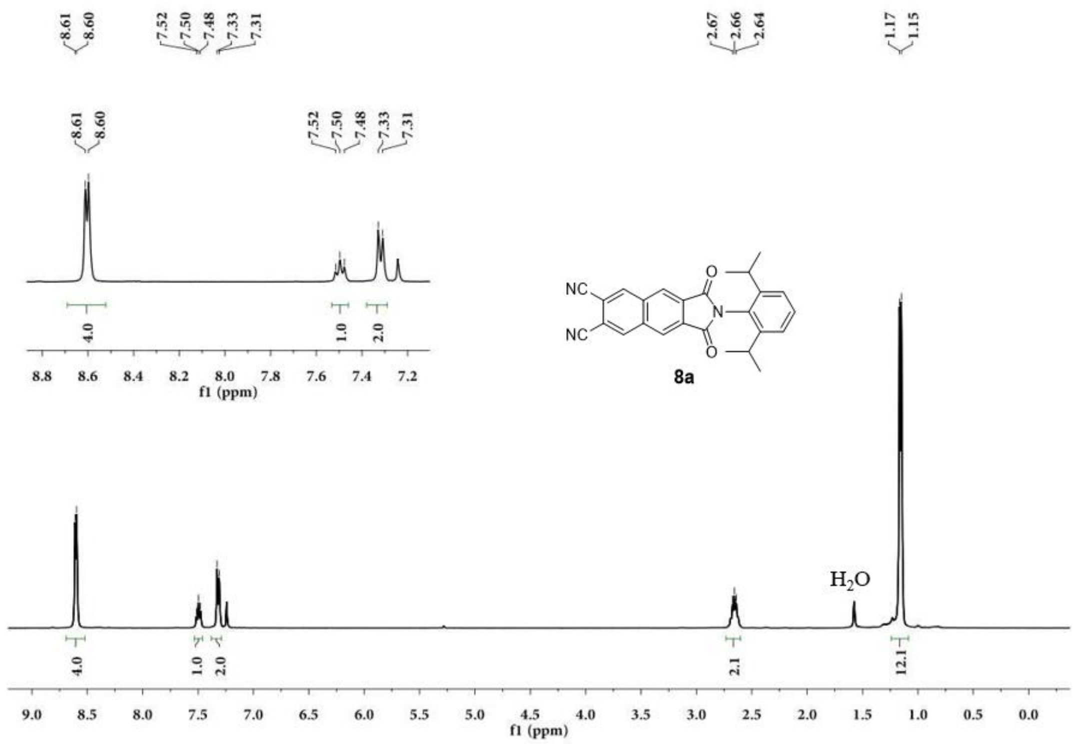
^1H NMR of compound **7b** in $CDCl_3$ (400 MHz)



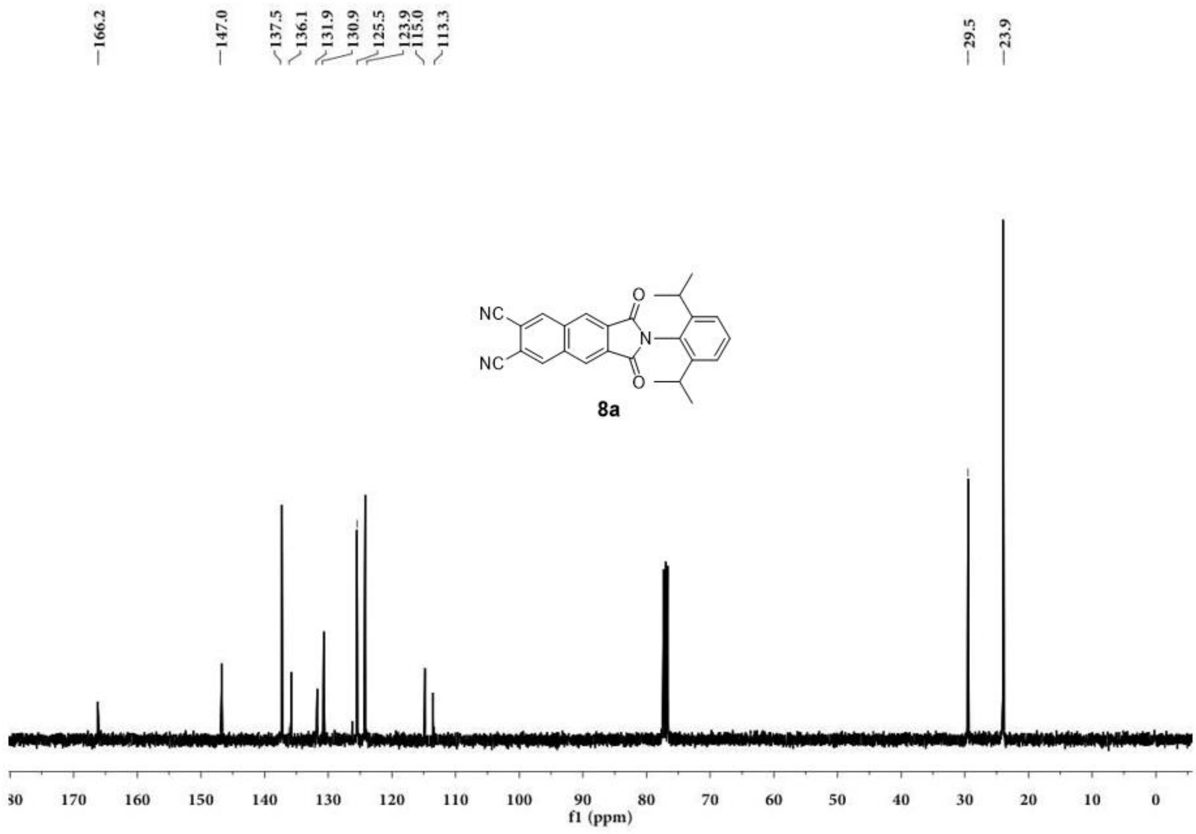
^{13}C NMR of compound **7b** in $CDCl_3$ (101 MHz)



^{1}H NMR of compound **8a** in $CDCl_3$ (400 MHz)



^{13}C NMR of compound **8a** in $CDCl_3$ (101 MHz)



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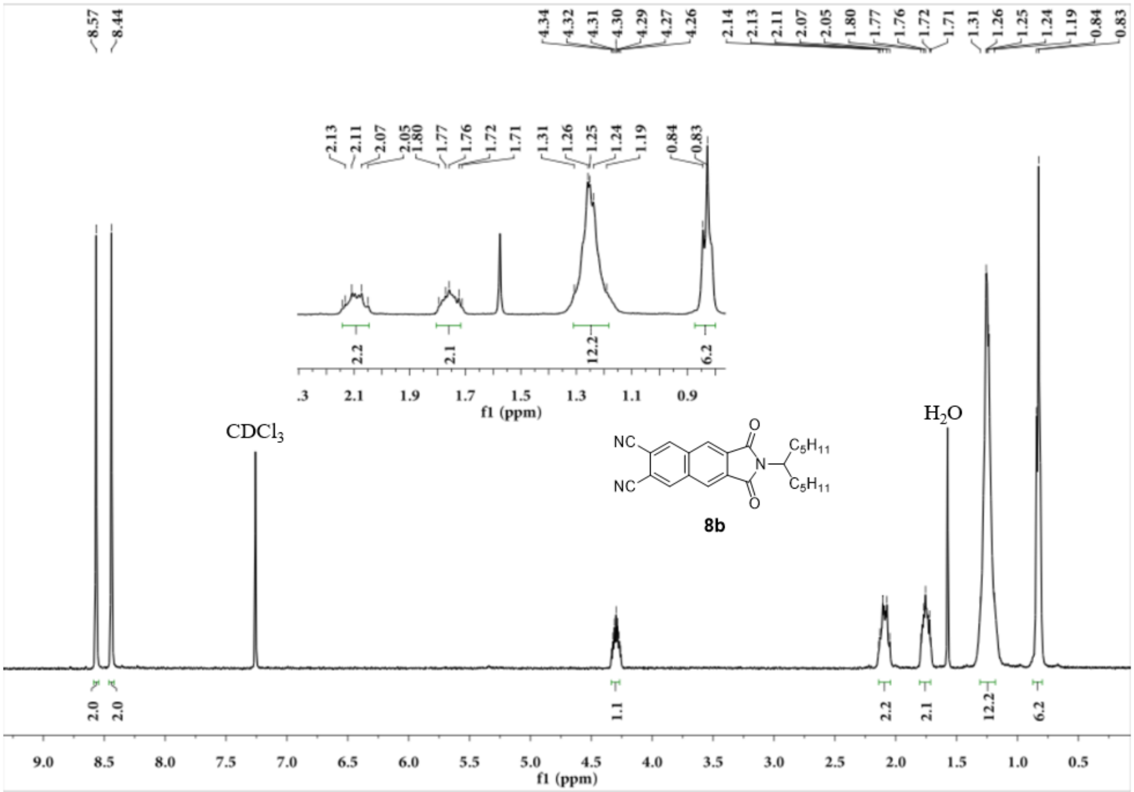

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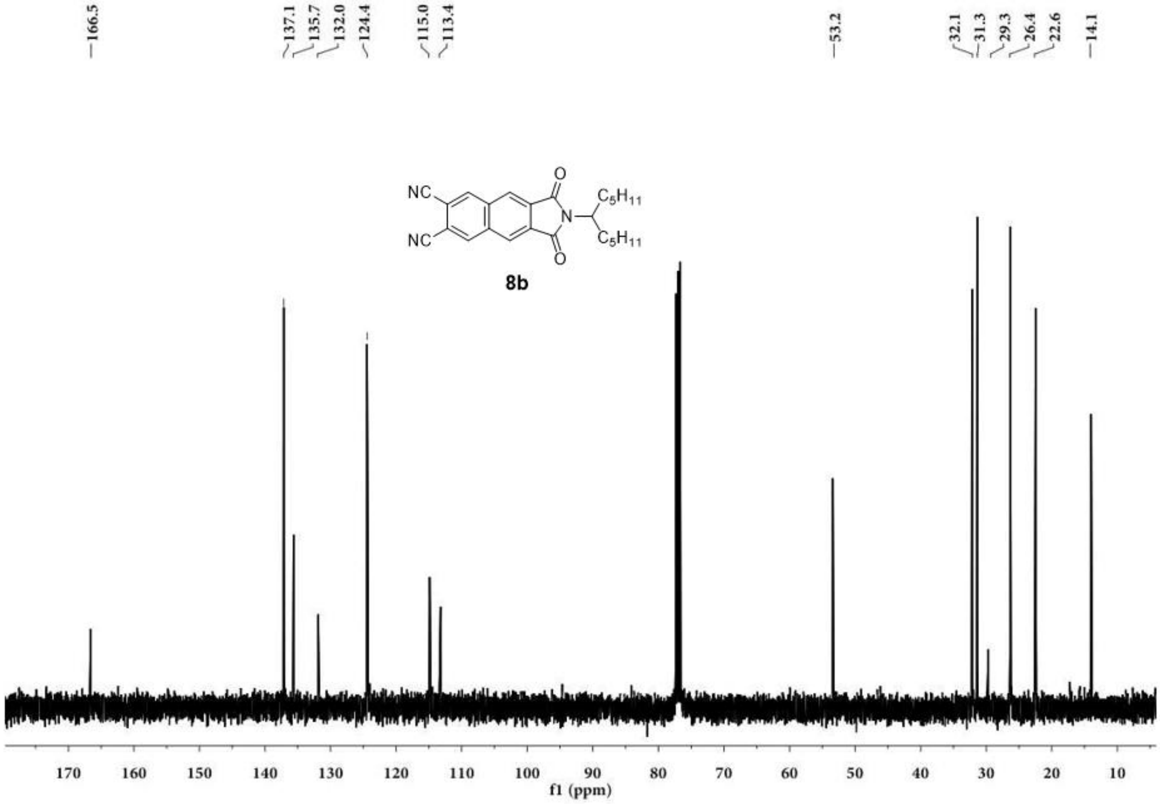
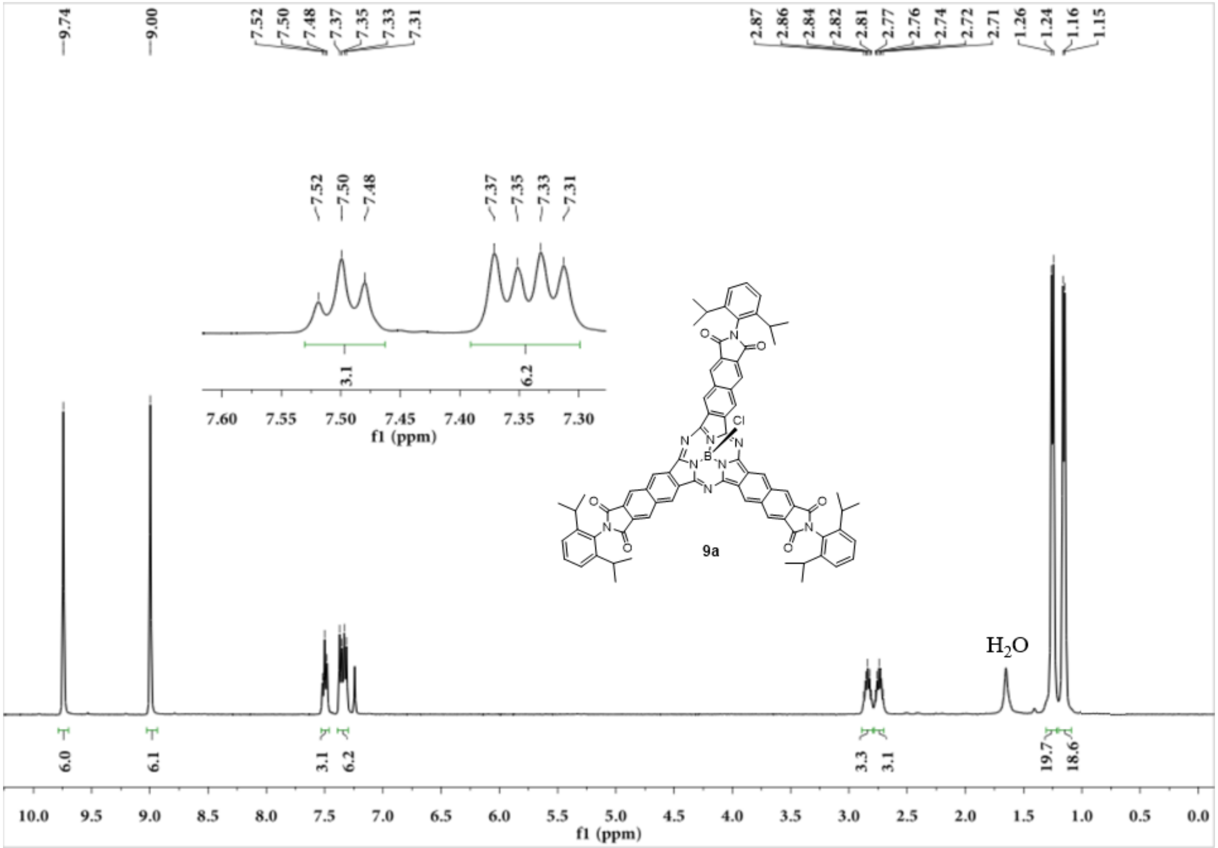
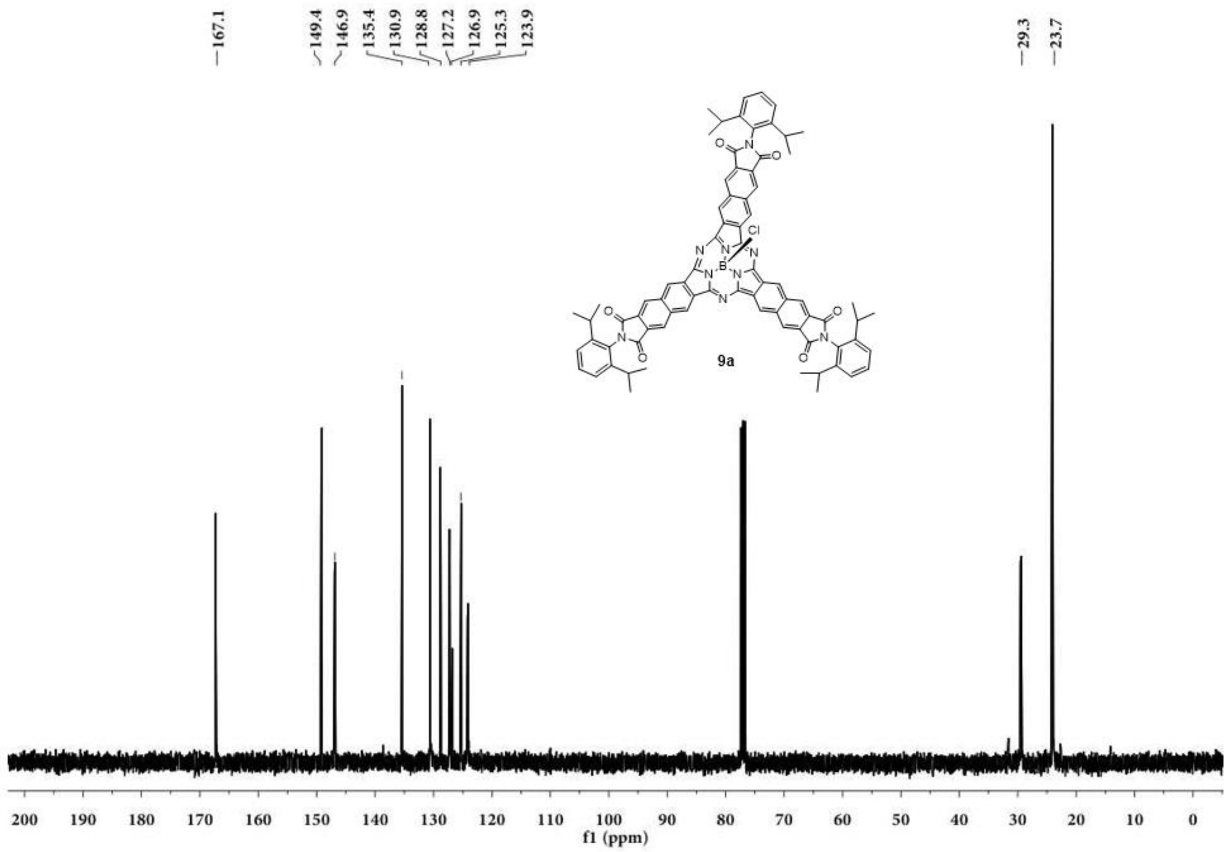


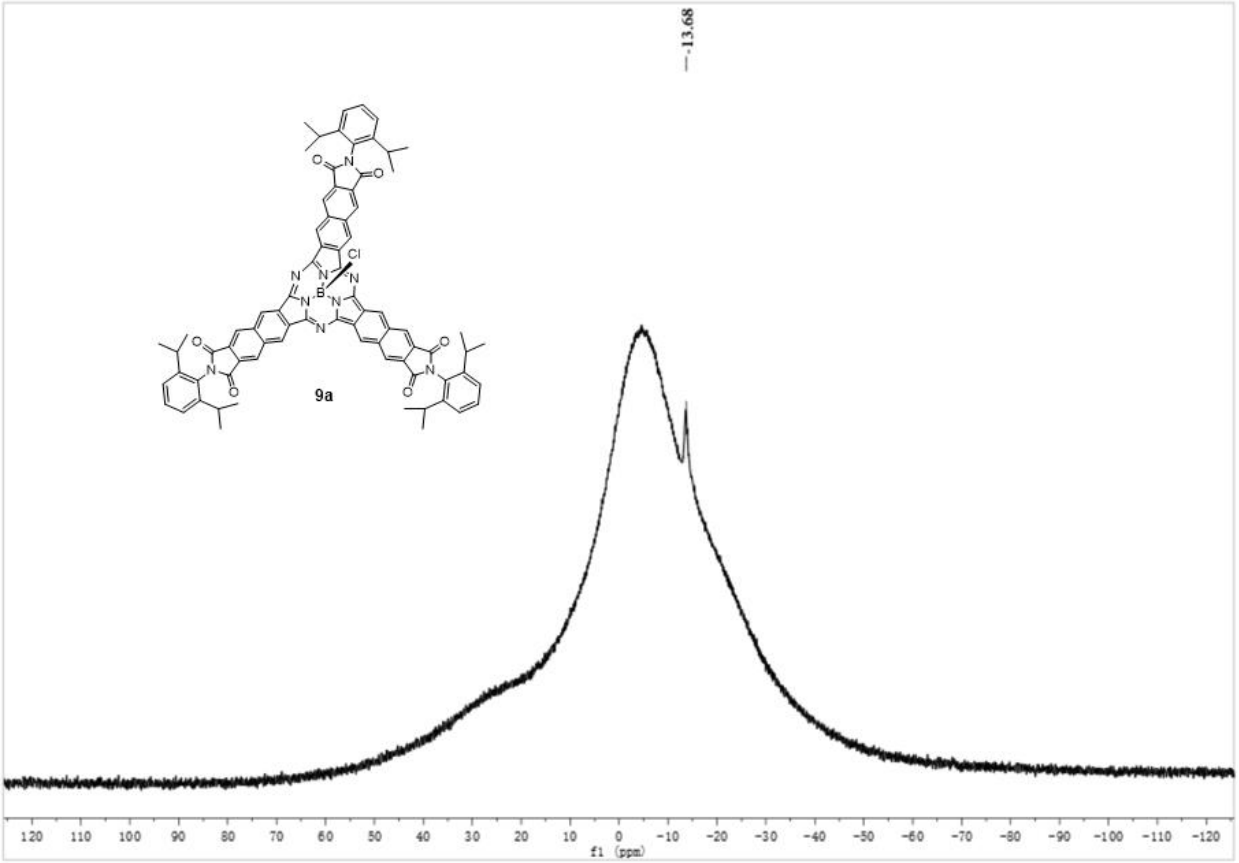
^1H NMR of compound **9a** in $CDCl_3$ (400 MHz)



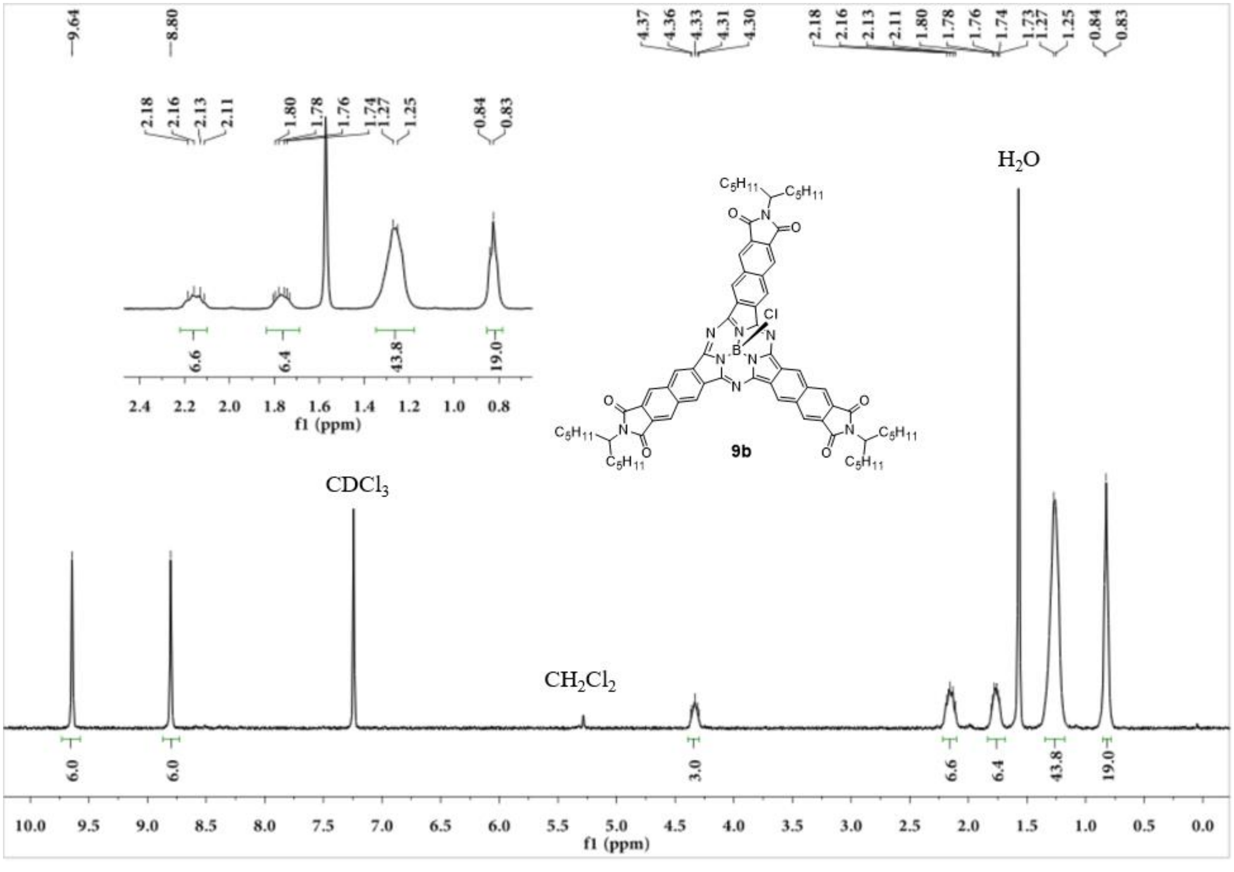
^{13}C NMR of compound **9a** in $CDCl_3$ (101 MHz)



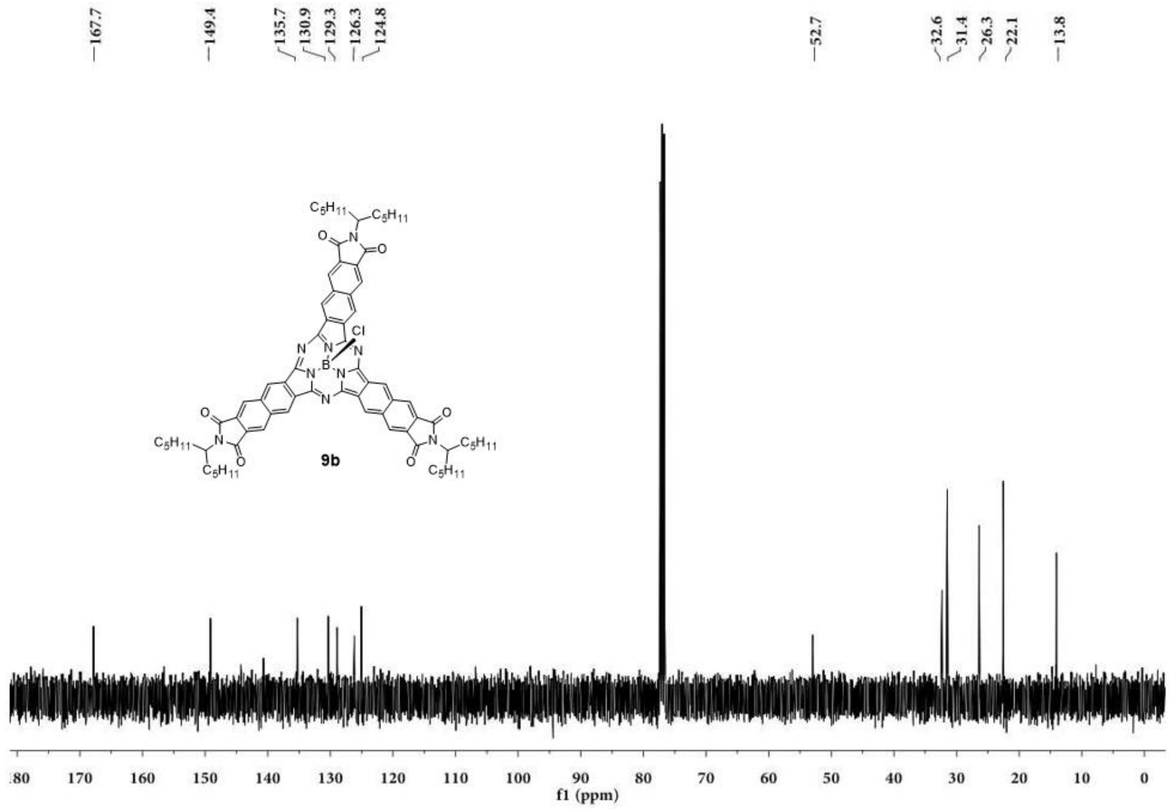
^{11}B NMR of compound **9a** in $CDCl_3$ (128 MHz)



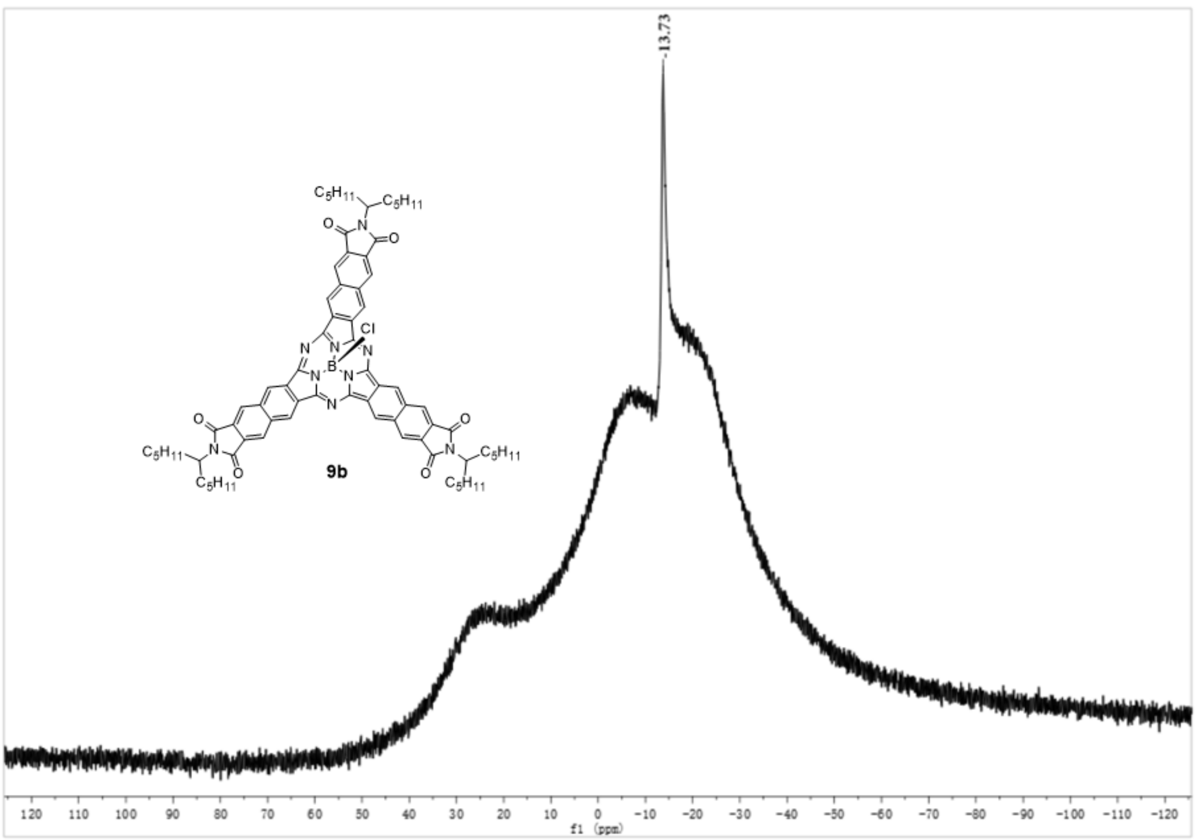
^{1}H NMR of compound **9b** in $CDCl_3$ (400 MHz)



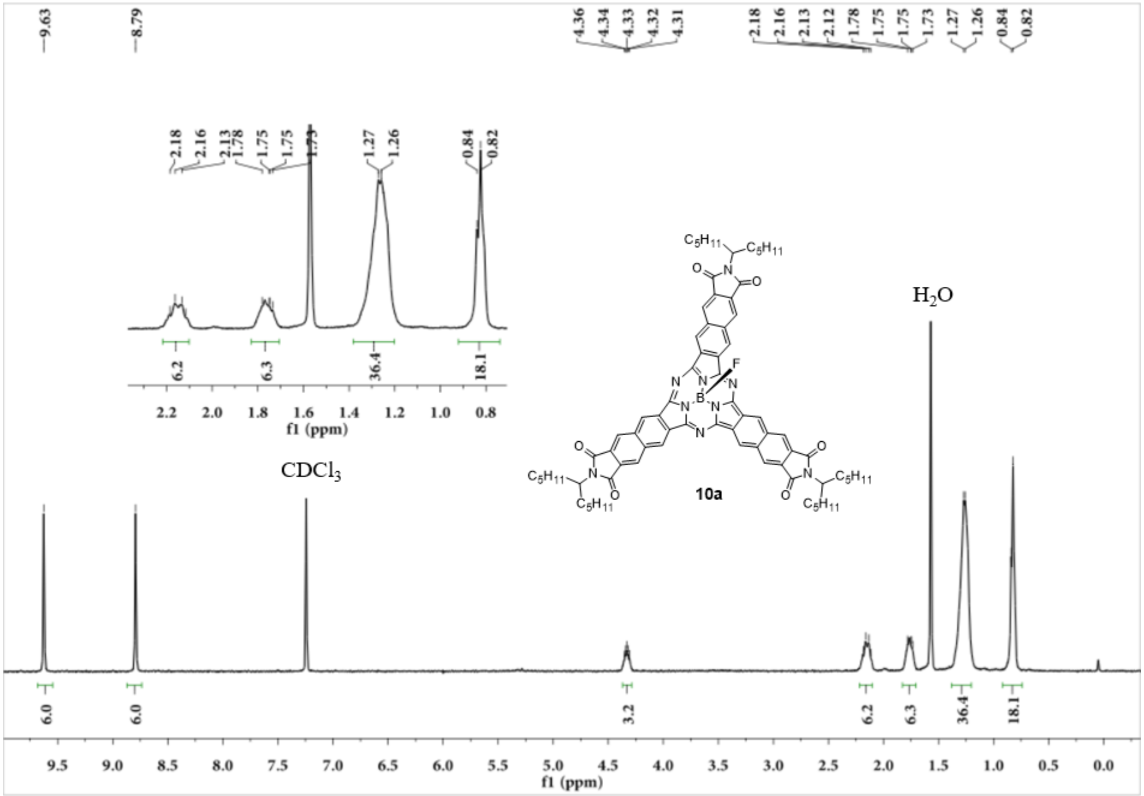
^{13}C NMR of compound **9b** in $CDCl_3$ (101 MHz)



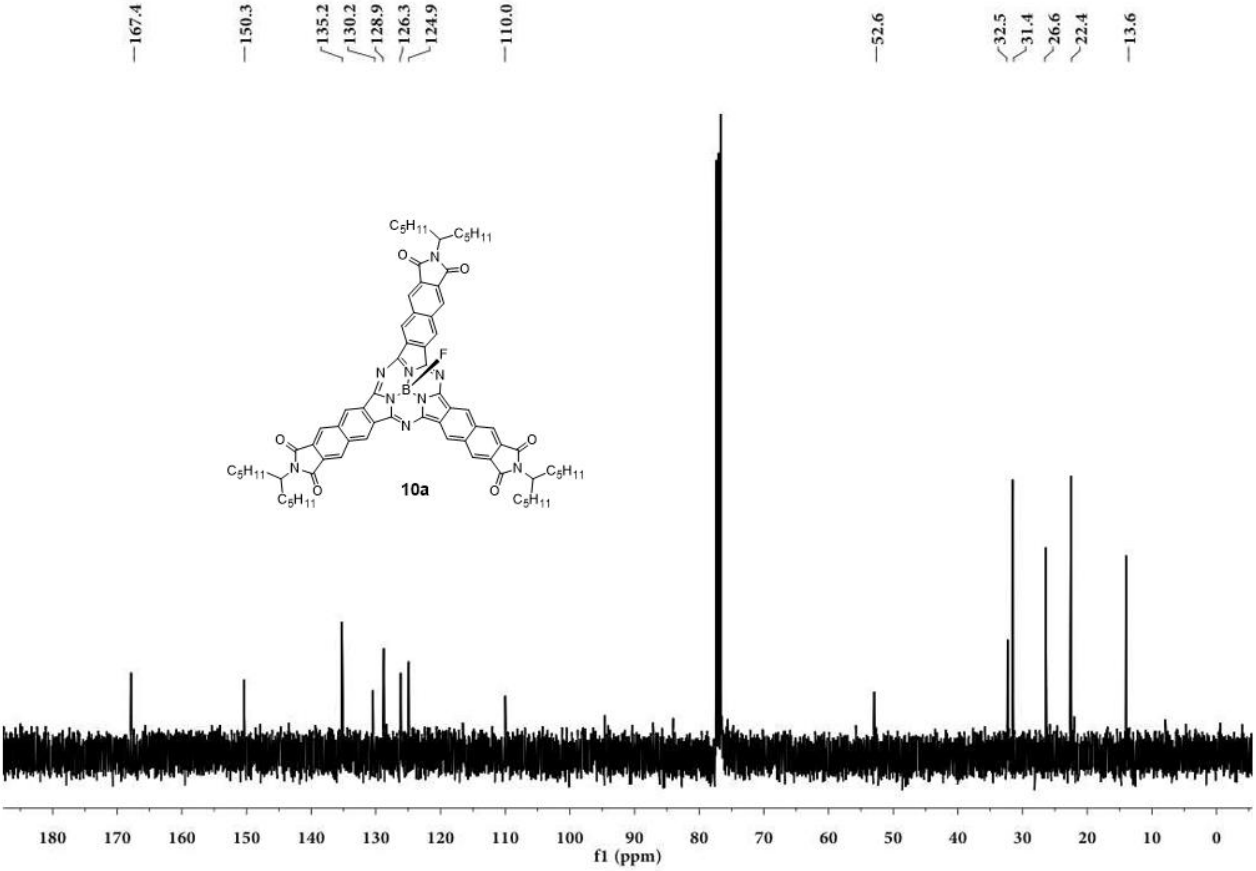
^{11}B NMR of compound **9b** in $CDCl_3$ (128 MHz)



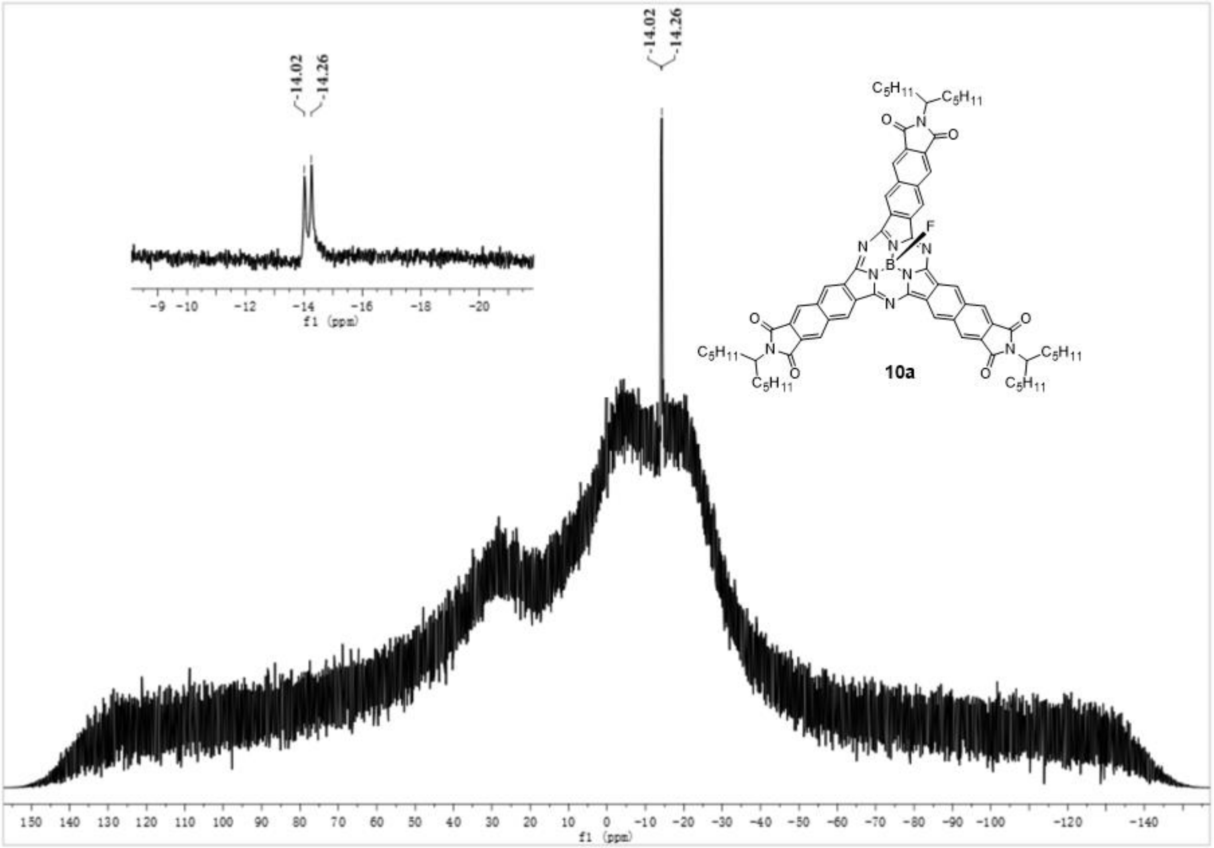
[1]H NMR of compound **10a** in $CDCl_3$ (400 MHz)



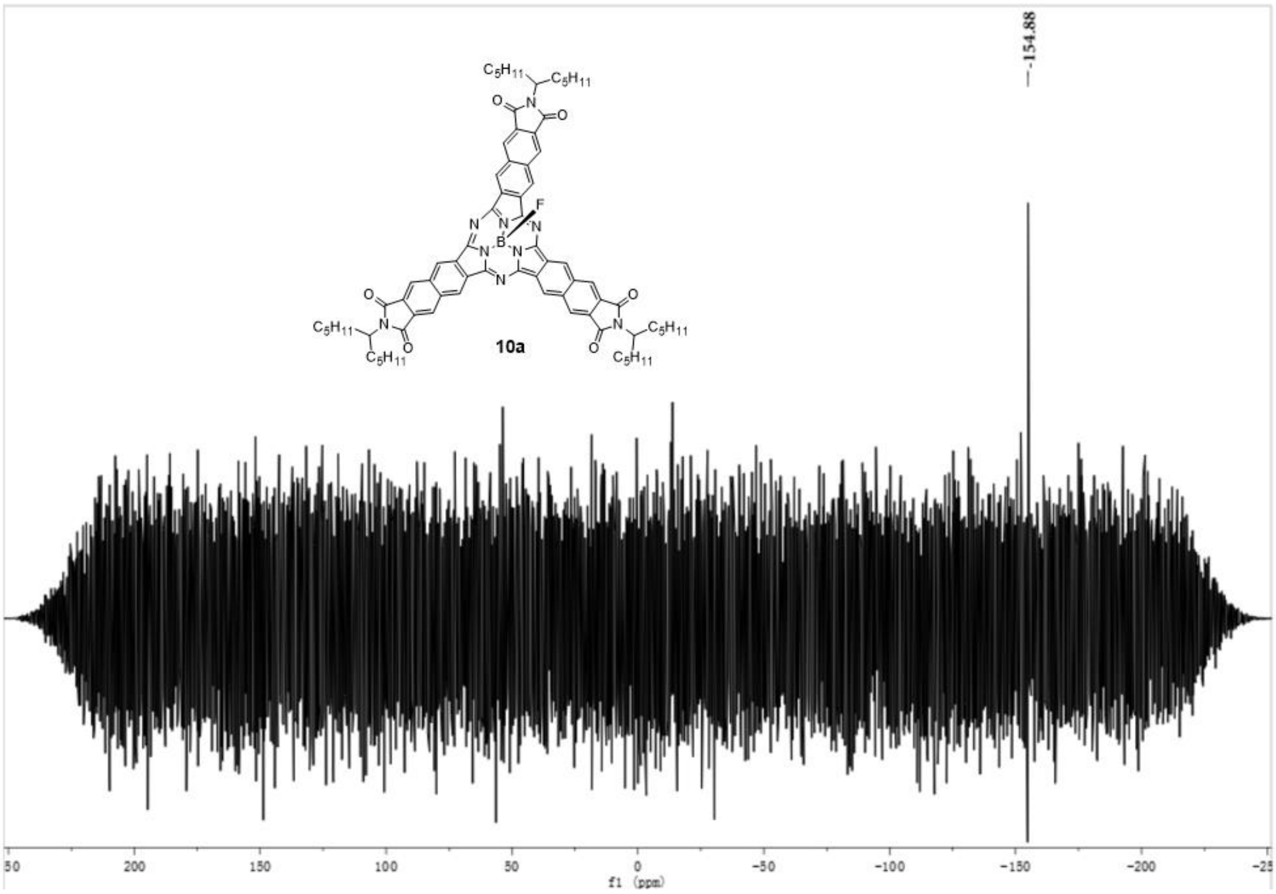
[13]C NMR of compound **10a** in $CDCl_3$ (101 MHz)



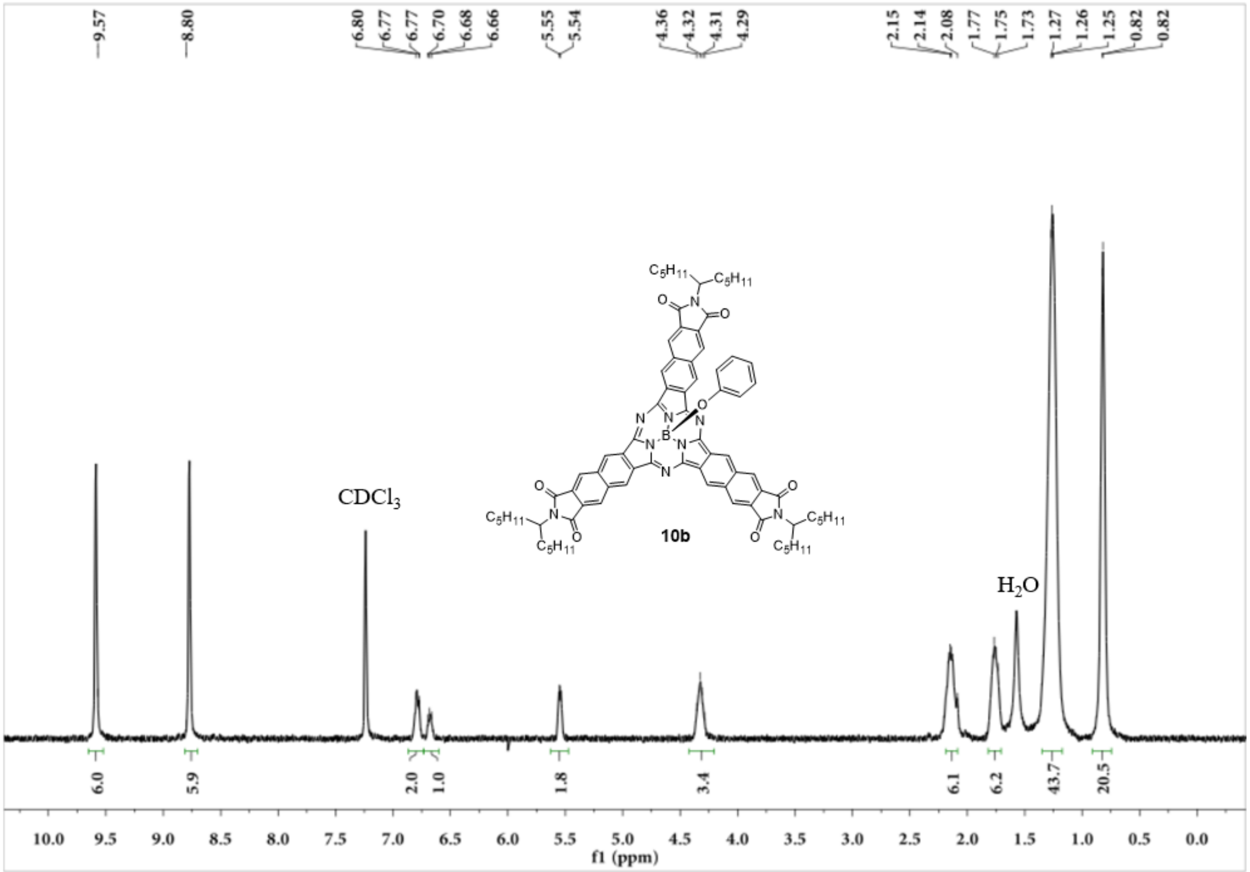
^{11}B NMR of compound **10a** in $CDCl_3$ (128 MHz)



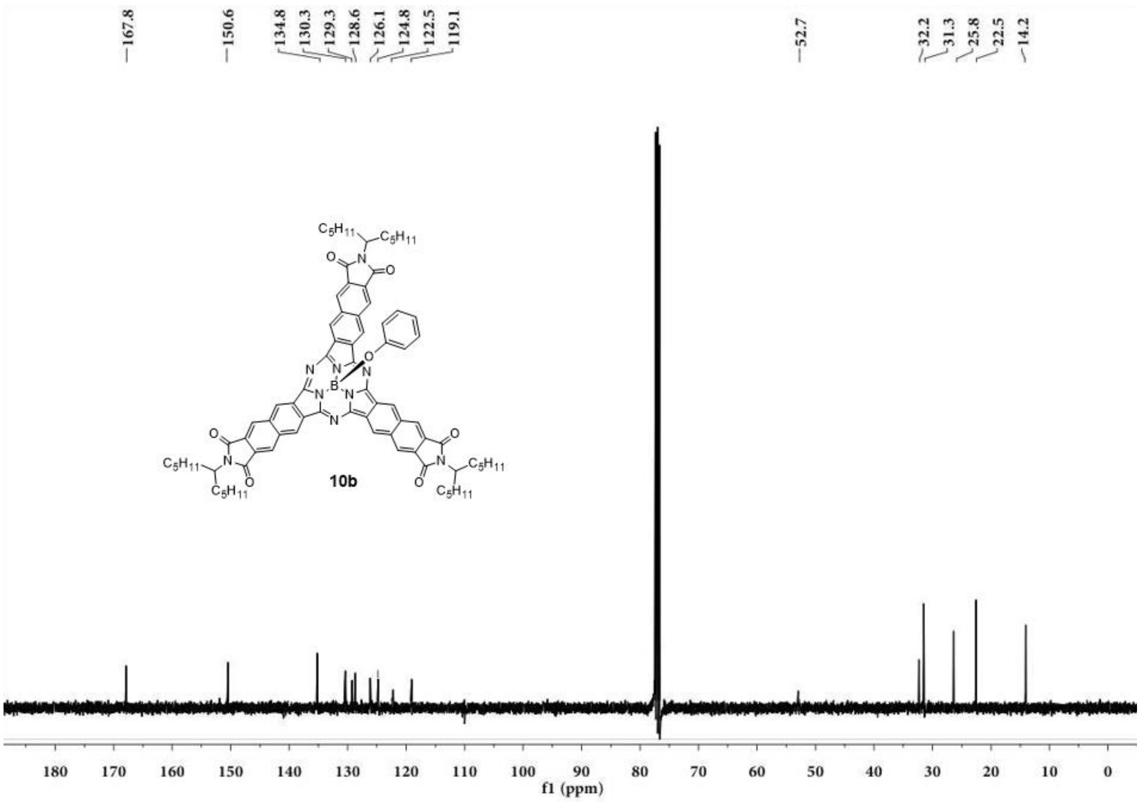
^{19}F NMR of compound **10a** in $CDCl_3$ (376 MHz)



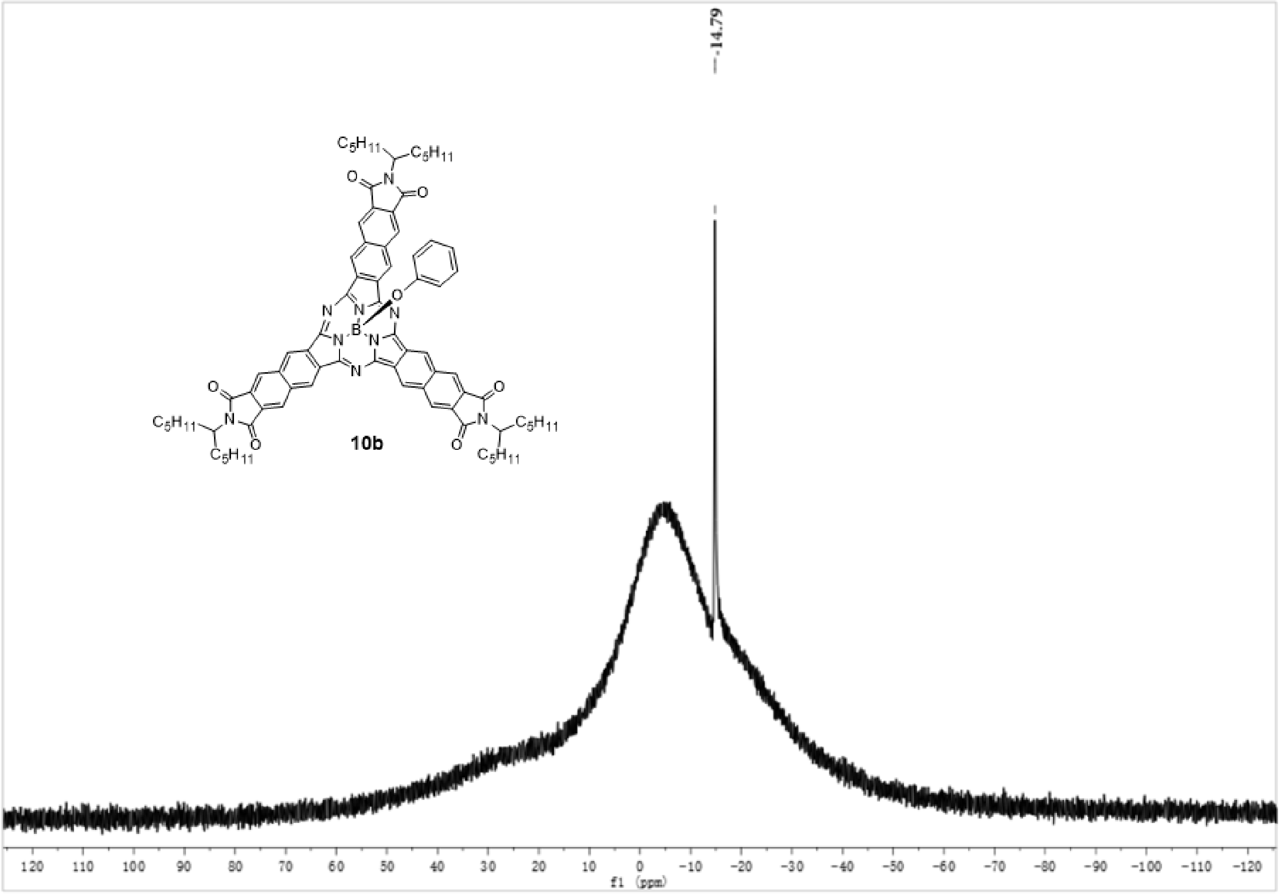
[1]H NMR of compound **10b** in $CDCl_3$ (400 MHz)



[13]C NMR of compound **10b** in $CDCl_3$ (101 MHz)



^{11}B NMR of compound **10b** in $CDCl_3$ (128 MHz)



15. References

1. Z. He, B. Xiao, F. Liu, H. Wu, Y. Yang, S. Xiao, C. Wang, T. P. Russell and Y. Cao, *Nat. Photon.*, 2015, **9**, 174-179.
2. S. Niu, Z. Liu and N. Wang, *Nanoscale*, 2018, **10**, 8483-8495.
3. H. Do Kim, R. Shimizu and H. Ohkita, *Chem. Lett.*, 2018, **47**, 1059-1062.
4. C. Sun, F. Pan, H. Bin, J. Zhang, L. Xue, B. Qiu, Z. Wei, Z.-G. Zhang and Y. Li, *Nat. Commun.*, 2018, **9**, 743.
5. H. Bin, Z.-G. Zhang, L. Gao, S. Chen, L. Zhong, L. Xue, C. Yang and Y. Li, *J. Am. Chem. Soc.*, 2016, **138**, 4657-4664.
6. G. Malliaras, J. Salem, P. Brock and C. Scott, *Phys. Rev. B*, 1998, **58**, R13411.
7. Y. Changduk, P. Hyesung, C. Shanshan, J. Sungwoo, C. H. Jin, K. Na-Hyang, J. Seungon, X. Jianqiu, O. Jiyeon and C. Yongjoon, *Angew. Chem. Int. Ed.*, 2018, **57**, 13277-13282.
8. V. D. Mihailetchi, H. Xie, B. de Boer, L. A. Koster and P. W. Blom, *Adv. Funct. Mater.*, 2006, **16**, 699-708.
9. P. Schilinsky, C. Waldauf and C. J. Brabec, *Appl. Phys. Lett.*, 2002, **81**, 3885-3887.

16. Author contributions

Z. Yuan designed target compounds and synthesis. Y. Chen, Y. Zhang, and M. Hu gave advises on the device fabrication and characterization. C. Yang and S. Chen provided GIWAXS measurement and analysis. X. Zhao did theoretical calculations. Y. Hu gave advises on the synthesis. C. Cai did experiments on the synthesis, characterization of compounds, and device fabrication. L. Li and X. Huang did part of synthesis. C. Cai and Z. Yuan wrote the draft. Y. Chen, C. Yang, S. Chen, M. Hu, X. Huang and X. Chen edited the manuscript.

Z. Yuan, design and advise: lead; project administration: lead; writing-review & editing: lead
Y. Chen, device fabrication and characterization: lead; editing-original draft: lead
C. Yang and S. Chen, GIWAXS measurement and analysis: lead; editing-original draft: lead
X. Zhao, theoretical calculation of molecules: lead
Y. Zhang, device fabrication and characterization: supporting
Y. Hu, advise on synthesis: supporting
C. Cai, synthesis, characterization, and device fabrication: lead; writing-review & editing: lead
L. Li, synthesis and characteriztion: equal
M. Hu, device fabrication and characterization: supporting; editing-original draft: supporting
X. Huang, synthesis and characteriztion: supporting; editing-original draft: supporting
X. Chen, editing-original draft: supporting.