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

ESI for: 2-Bromo perylene diimide: synthesis using C–H activation and use in the synthesis of bis(perylene diimide)-donor electron-transport materials

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Supporting Information

Contents

1. Materials and General Methods

^{1}H and $^{13}C\{1H\}$ NMR spectra were acquired using a Bruker AMX-400 spectrometer or Varian Mercury Vx 300, and the signals were referenced to residual solvent peak (7.27 ppm for ^{1}H NMR and 77.0 ppm for ^{13}C NMR) or internal standard TMS (0.0 ppm).

Chromatographic separations were performed using standard flash column chromatography methods using silica gel purchased from Sorbent Technologies (60 Å, 32-63 μm). Electrochemical measurements were carried out under nitrogen in dry deoxygenated 0.1 M tetra-*n*-butylammonium hexafluorophosphate in dichloromethane (ca. 10^{-4} M of analyte) using a conventional three-electrode cell with a glassy carbon working electrode, platinum wire counter electrode, and a Ag wire coated with AgCl as pseudo-reference electrode. Potentials were referenced to ferrocenium/ferrocene. Cyclic voltammograms were recorded at a scan rate of 50 $mV.s^{-1}$. UV-vis-NIR spectra were recorded in 1 cm cells using a Varian Cary 5E spectrometer. Mass spectra were recorded on an Applied Biosystems 4700 Proteomics Analyzer by the Georgia Tech Mass Spectrometry Facility. Elemental analyses were performed by Atlantic Microlabs. Differential scanning calorimetry measurements were taken on a Q200 Differential Scanning Calorimeter (TA Instruments, New Castle, DE), at 10 °C min^{-1}, with 50 mL min^{-1} N_2 flow, with total organic solids weight of ca. 5 mg.

Table 1. Conditions tried for the Ir- or Ru-catalysed direct monoborylation of **PDI**

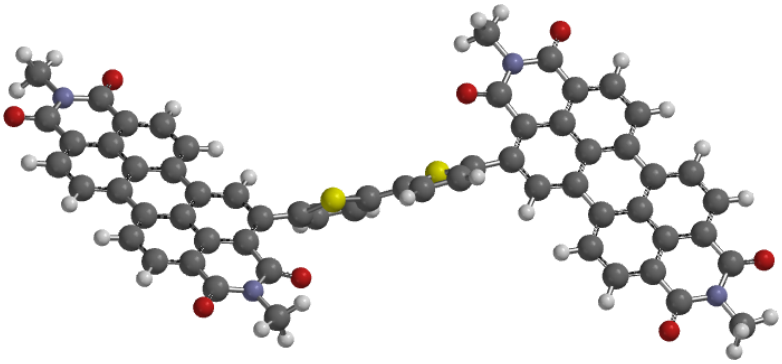
Entry	TM Catalyst	B_2Pin_2	Solvent	Temperature (°C)	Yield of PDI-Bpin (isolated)
1	$[Ir(OMe)cod]_2$[a] (3 mol%) $P(C_6F_5)_3$ (12 mol%)	1.5 eq	dioxane	120	35%
2	$[Ir(OMe)cod]_2$ (3 mol%) $P(C_6F_5)_3$ (12 mol%)	1.0 eq	dioxane	110	~11%
3	$[Ir(OMe)cod]_2$ (3 mol%) $P(C_6F_5)_3$ (12 mol%)	2.0 eq	dioxane	110	~12%
4	$Ru(H)_2(CO)(PPh_3)_3$ (50 mol%)	8.0 eq	mesitylene/pinacolone	140	44%
5	$RuH_2(CO)(PPh_3)_3$ (10 mol%)	1.2 eq	mesitylene/pinacolone	140	38%

[a] cod = 1,5- cyclooctadiene

2. DFT molecular geometry optimisation

The neutral ground-state structures were obtained at the DFT (B3LYP/6-31G**) level for **7-9** and **PDI2-DTP-bay** with all *N,N'*-alkyl groups replaced by methyl groups to reduce computational cost.

7



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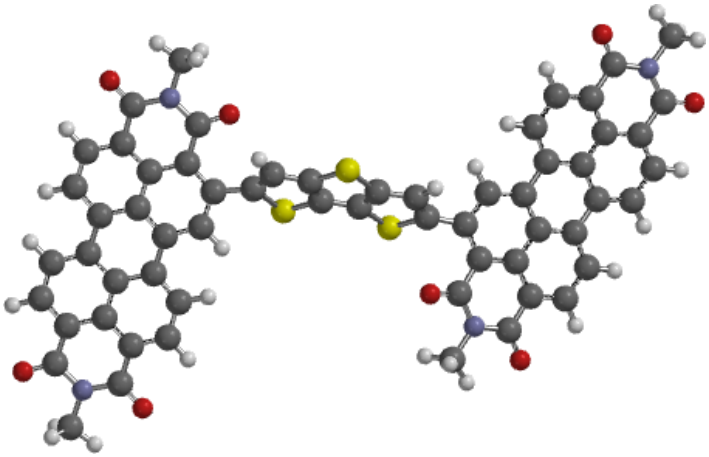

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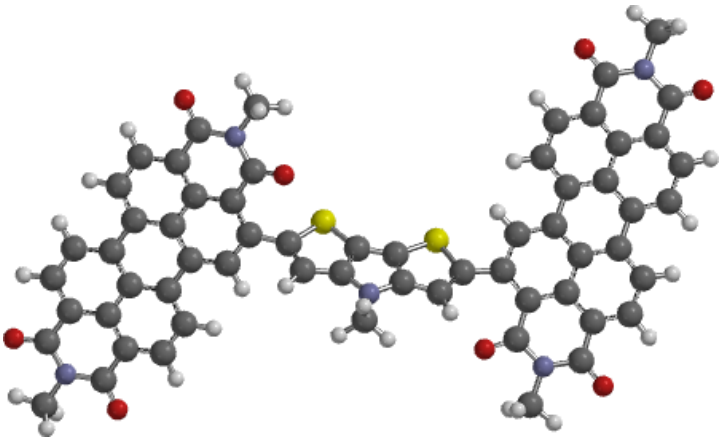

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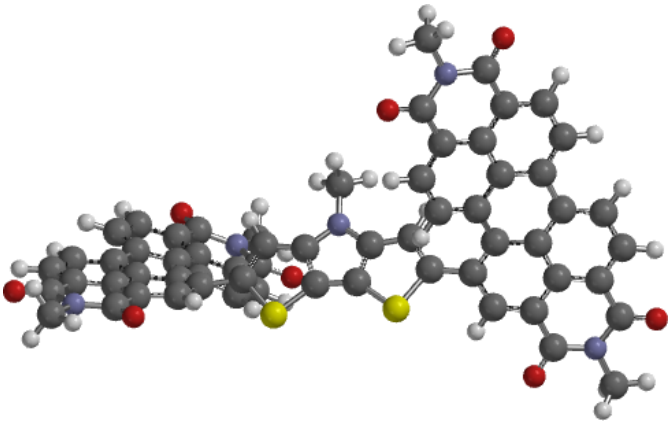


Figure S1. DFT-predicted (B3LYP/6-31G* level) conformations (side view) of **7-10**.

3. Electrochemical Properties

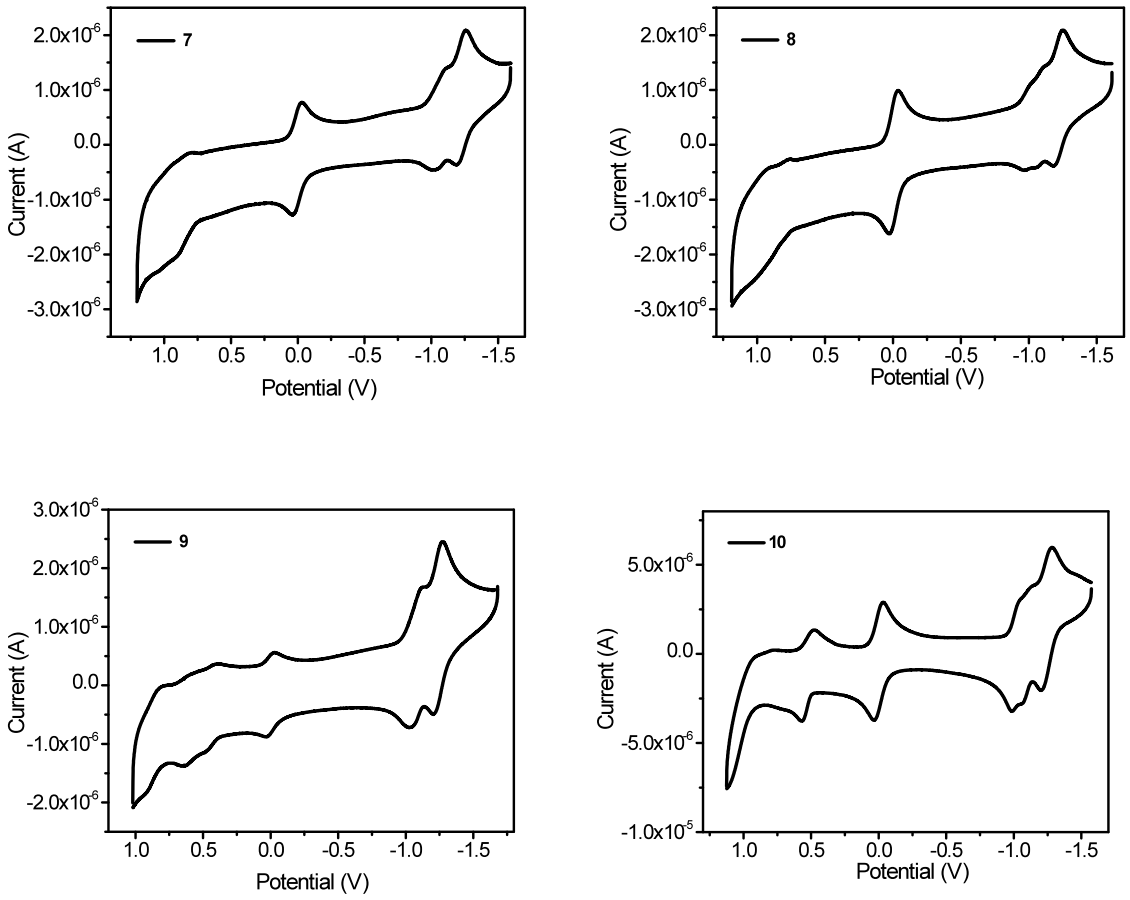


Figure S2. Cyclic voltammograms of **7-10** conducted in 0.1 M $^{n}Bu_4NPF_6$ in CH_2Cl_2 with $Cp_2Fe^{+/0}$ as internal reference at a scan rate of 50 mV s^{-1}.

4. Thermal Characterisation

Differential scanning calorimetry (DSC, Figure S3) indicating melting points of ca. 248.5 °C and 260.3 °C for **7** and **8**, respectively; this indicates that the materials possess enough thermal stability for applications in thin film devices. Upon cooling, two corresponding exothermic transitions are observed at 243.5 °C and 219.2 °C, respectively. **9** solid shows no visible thermal transitions up to 350 °C.

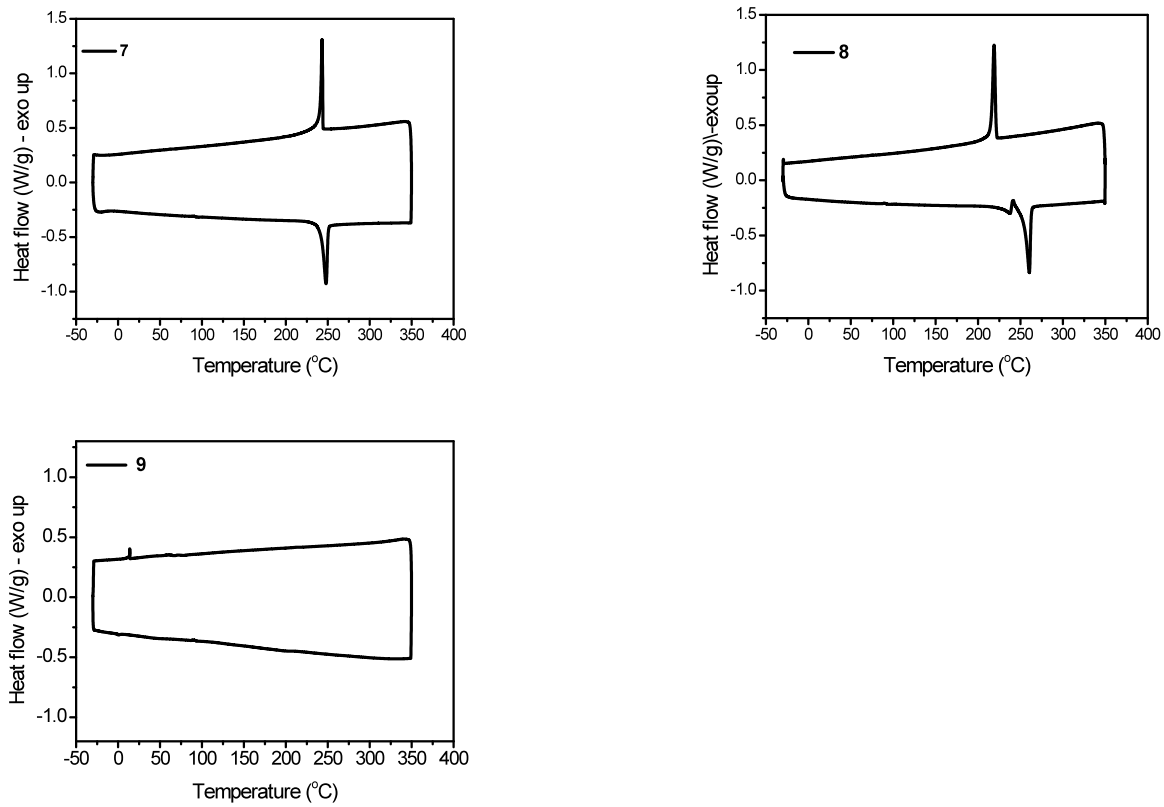


Figure S3. Second scanning differential scanning calorimetry plots of compounds **7**, **8**, and **9**.

5. OFET Fabrication and Properties

OFETs with bottom contact and top gate structure were fabricated on glass substrates (Eagle 2000 Corning). Au (50 nm) bottom contact source/drain electrodes were deposited by thermal evaporation through a shadow mask. Organic semiconductor layers were formed on the substrates by spin coating solution of **7-9** (10-15 mg mL^{-1}) at 500 rpm for 10 s and at 2000 rpm for 20 s. These organic layers were annealed at 100 °C for 15 min on the hot plate inside a nitrogen glove box. CYTOP (45 nm)/Al_2O_3 (50 nm) bilayers was used as top gate dielectrics. CYTOP solution (CTL-809M) was purchased from Asahi Glass with a concentration of 9 wt. %. To deposit the 45-nm-thick fluoropolymer layers, the original solution was diluted (CT-solv.180, Asahi glass) to give solution:solvent ratios of 1:3.5. CYTOP layers were deposited by spin coating at 3000 rpm for 60 s. Al_2O_3 (50 nm) films were deposited on fluoropolymer layers by atomic layer deposition at 110 °C using alternating exposures of $AlMe_3$ and H_2O vapor at a deposition rate of approximately 0.1 nm per cycle. All spin coating and annealing processes were carried out in a N_2-filled dry box. Finally, Al (150 nm) gate electrodes were deposited by thermal evaporation through a shadow mask.

Bottom gate and top contact OFETs were fabricated on heavily doped n-type silicon substrates (resistivity < 0.005 Ωcm, also serve as gate electrodes) with 200 nm thick thermally grown SiO_2 as the gate dielectric. Firstly, the substrates were cleaned by O_2 plasma for two minutes. The SiO_2 dielectric surface was then passivated with a thin buffer layer of BCB (Cyclotene^{TM}, Dow Chemicals), to provide a high-quality hydroxyl-free interface. The BCB was in diluted in trimethylbenzene with the ratio 1:20, and spincoated at 3000 rpm for 60 s to provide a very thin uniform layer (thickness was not measured, final capacitance density was measured). The samples were annealed at 250 °C for 1 h inside a N_2 glove box for crosslinking. The total capacitance density (C_{OX}) was measured from parallel-plate capacitors; it was found to be ca. 14.5 nF/cm^2. An organic layer was spin coated (500 rpm for 10 s and 2000 rpm for 20 s) from solutions of **7-9 (**10 - 17 mg mL^{-1}) in designated solvents. Finally, Al (150 nm) was deposited through a shadow mask to act as source/drain electrodes.

All current-voltage (I-V) characteristics of OFETs were measured with an Agilent E5272A source/monitor unit in a N_2-filled glove box (O_2, H_2O < 0.1 ppm).

Table S2. Summary of top-gate bottom-contact OFETs and bottom-gate top-contact OFETs

Compound	C_{in} **(nF cm^{-2})**	**Solvent**	**S/D electrode**	μ **(cm^2 V^{-1} s^{-1})**	V_{TH} **(V)**	$I_{on/off}$
8[a]	35.2	DCB	Au	$1.27(\pm0.04)\times10^{-2}$	4.2 ±0.5	5×10^3
7[a]	35.2	$CHCl_3$	Au	$2.9(\pm0.7)\times10^{-3}$	4.9(±0.6)	1×10^3
7/PS[a] (1:1)	35.2	DCB	Au/Ti	$2.4(\pm1.7)\times10^{-2}$	5(±1)	4×10^4
8[b]	14.5	DCB	Al	$1.8(\pm0.3)\times10^{-3}$	3.5(±0.2)	1×10^4
8[b]	15.0	$CHCl_3$	Al	$1.4(\pm0.1)\times10^{-3}$	1.3(±0.1)	1×10^4
7[b]	15.0	$CHCl_3$	Al	$4.0(\pm0.5)\times10^{-3}$	0.7(±0.4)	1×10^4

[a]: top-gate bottom-contact OFET, W/L: 2550 μm/180 μm (avg. 8 devices)
[b]: bottom-gate top-contact OFET, W/L: 1200 μm/100 μm (avg. 4 devices)

6. X-ray Characterisation of Films

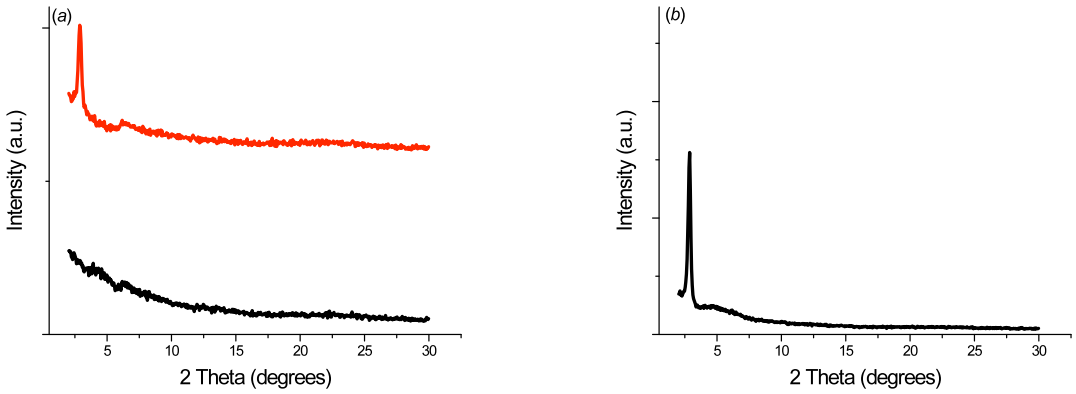


Figure S4. (a) XRD patterns of neat **7** films spin-coated onto glass substrates (Eagle 2000 Corning) from 1,2-dichlorobenzene (DCB) (above) and chloroform (below); (b) XRD pattern of neat **8** thin films spin-coating from 1,2-dichlorobenzene. The films cast from dichlorobenzene are somewhat crystalline, with Bragg peaks corresponding to *d*-spacings of 30.2° and 30.7° being seen for **7** and **8**, respectively, while the film cast from chloroform shows no evidence of crystallinity.

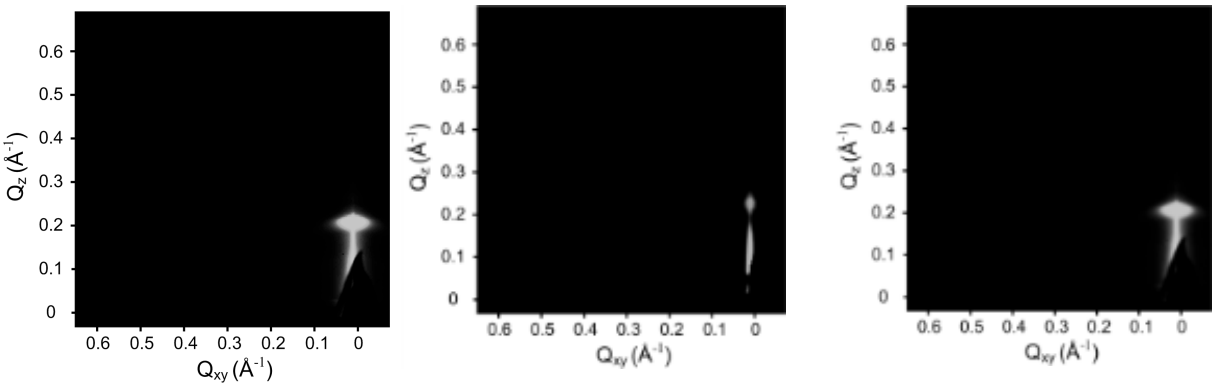
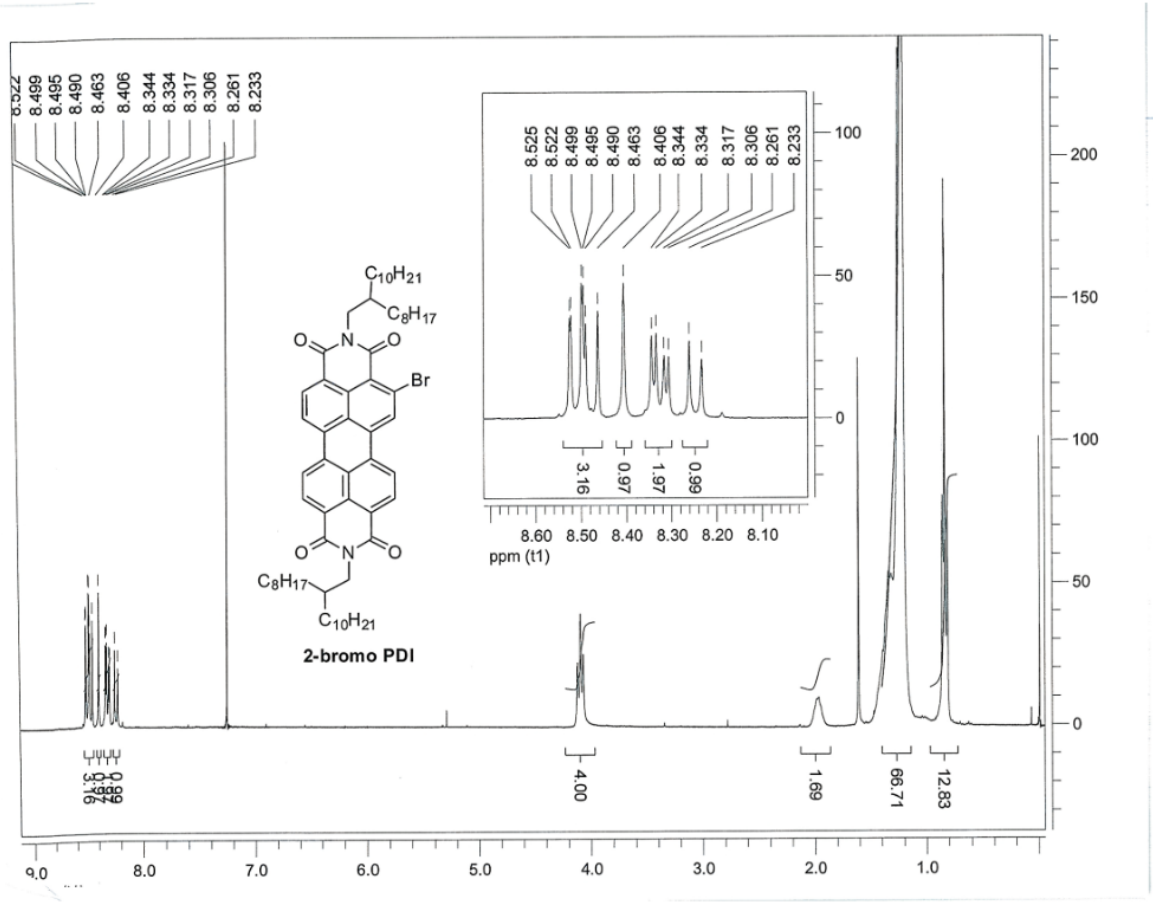


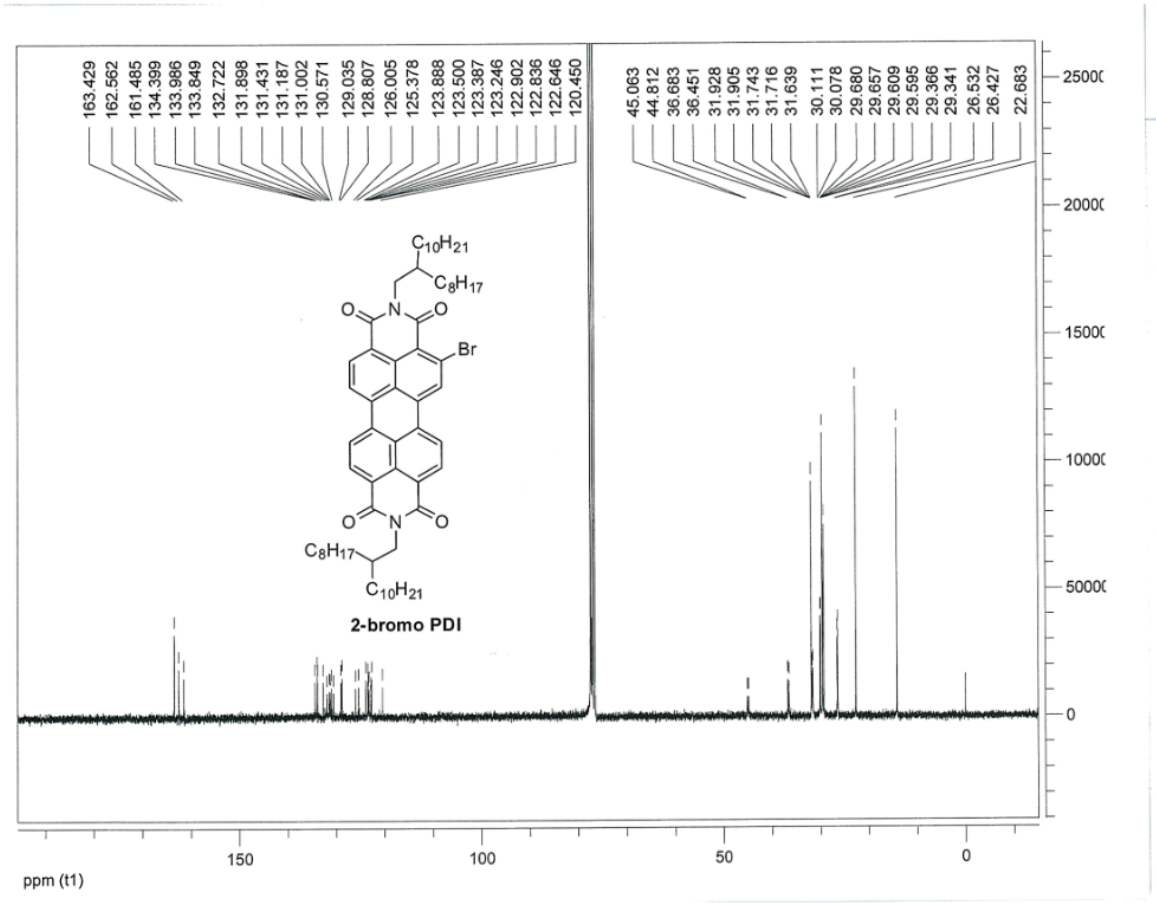
Figure S5. Grazing incidence wide angle x-ray scattering (GIWAXS) of thin films of triads coated onto glass substrates (Eagle 2000 Corning): **7** from DCB (left), **7** from chloroform (center), and **8** from DCB (right).

7. NMR Spectra of New Compounds

Compound **2**



Compound **2**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162.562
161.485
134.399
133.986
133.849
132.722
131.898
131.431
131.187
131.002
130.571
129.035
128.807
126.005
125.378
123.888
123.500
123.387
123.246
122.902
122.836
122.646
120.450
45.063
44.812
36.683
36.451
31.928
31.905
31.743
31.716
31.639
30.111
30.078
29.680
29.657
29.609
29.595
29.366
29.341
26.532
26.427
22.683
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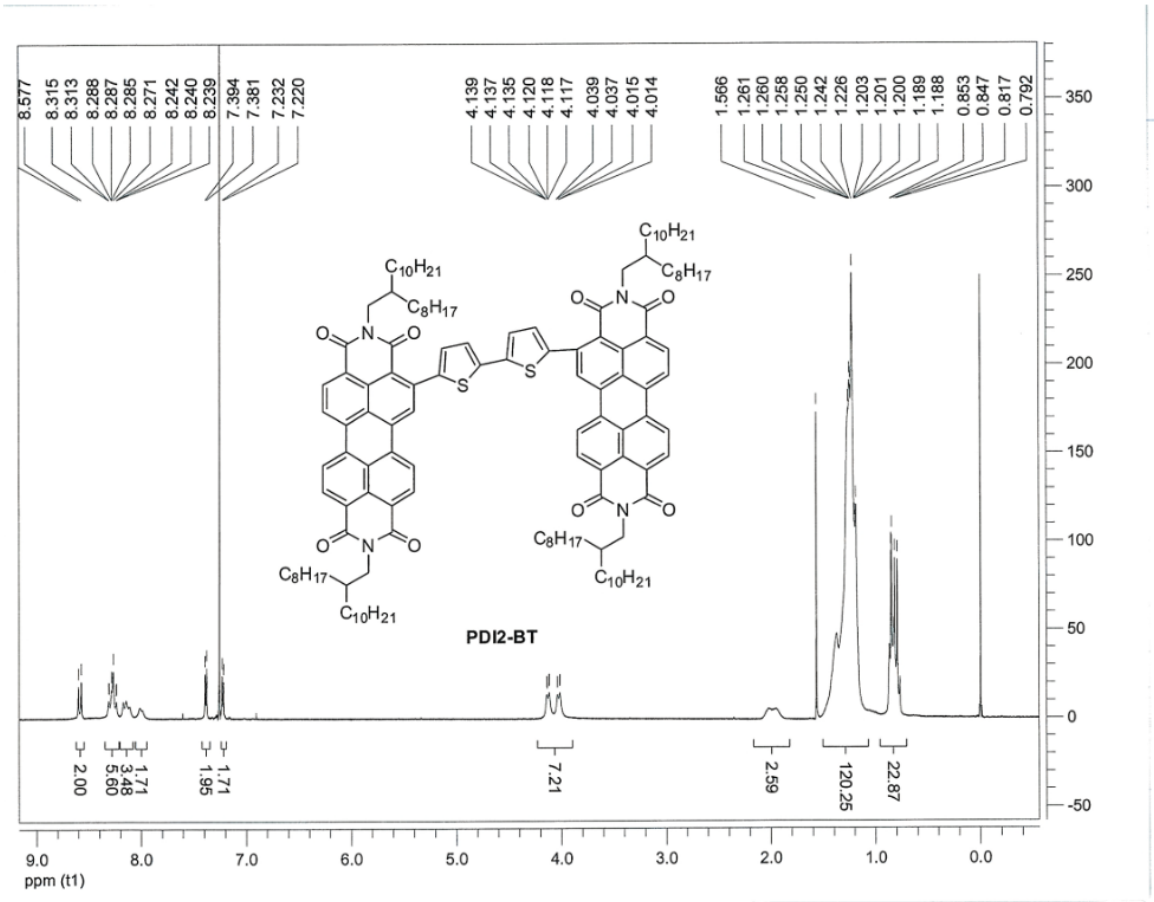
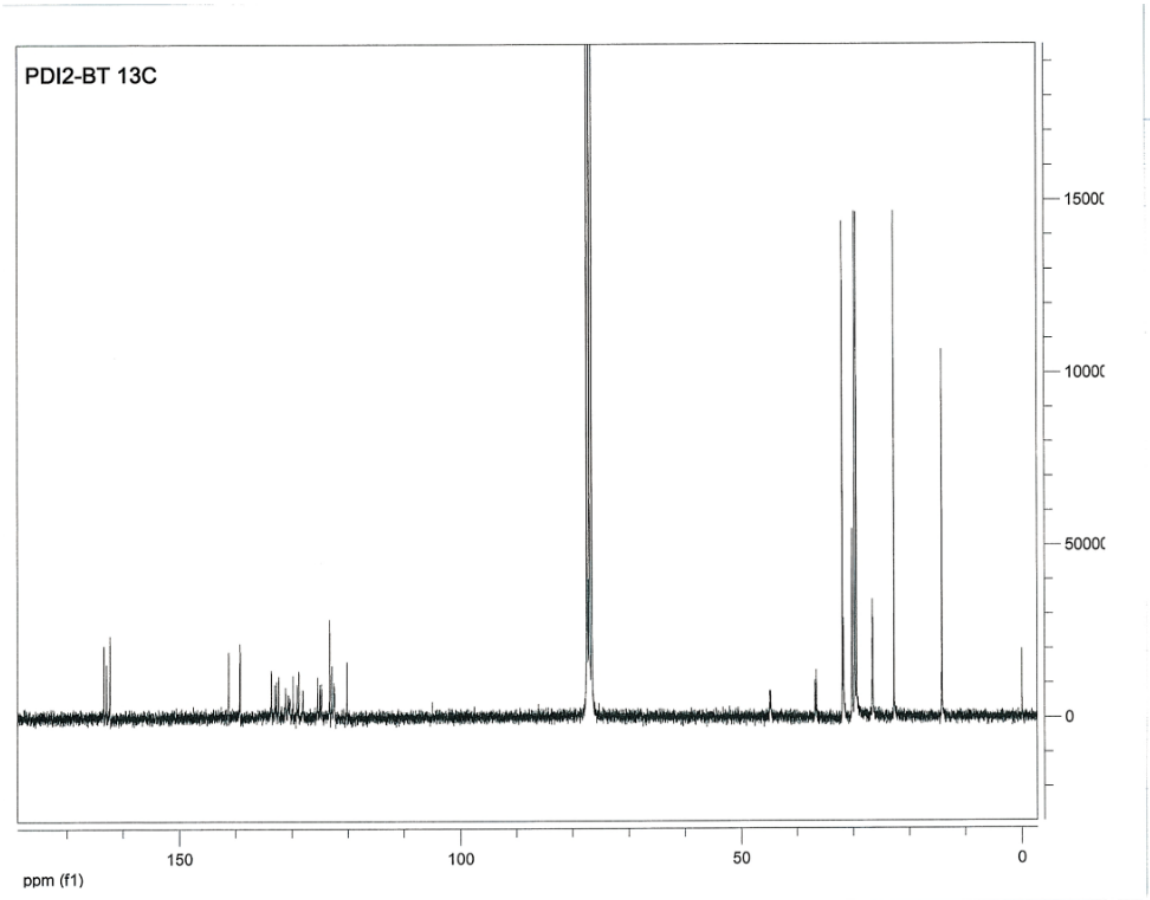
2000
1500
1000
5000
0
Br
2-bromo PDI
150
100
50
0
ppm (t1)

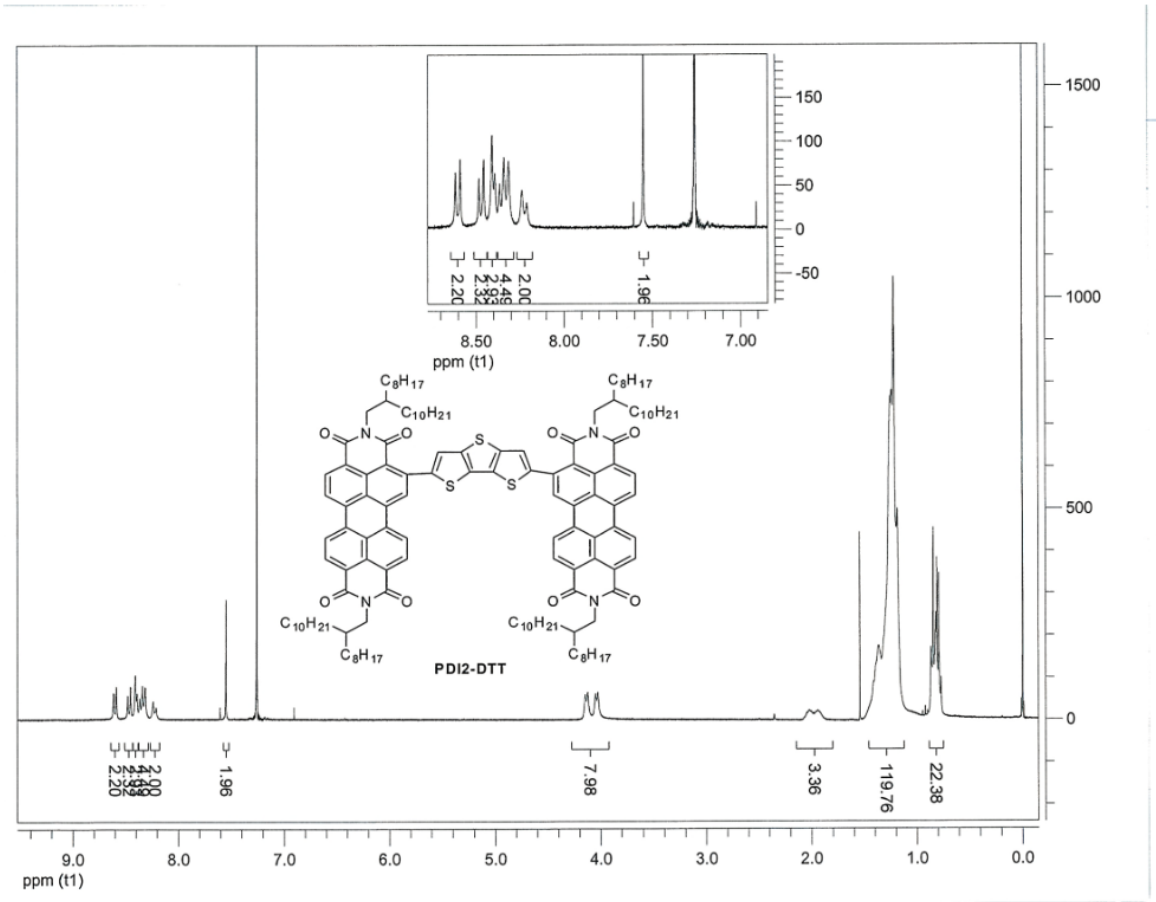
Compound **7**



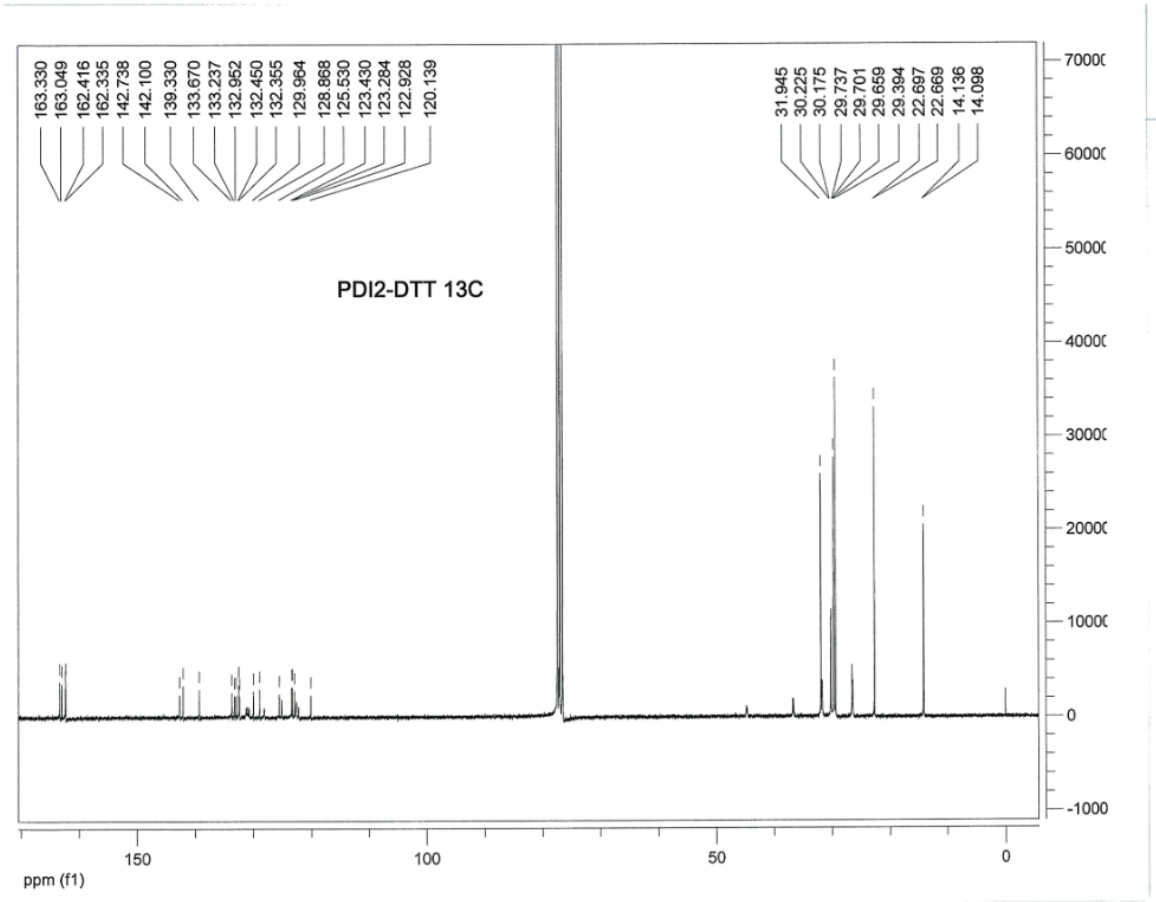
Compound **7**



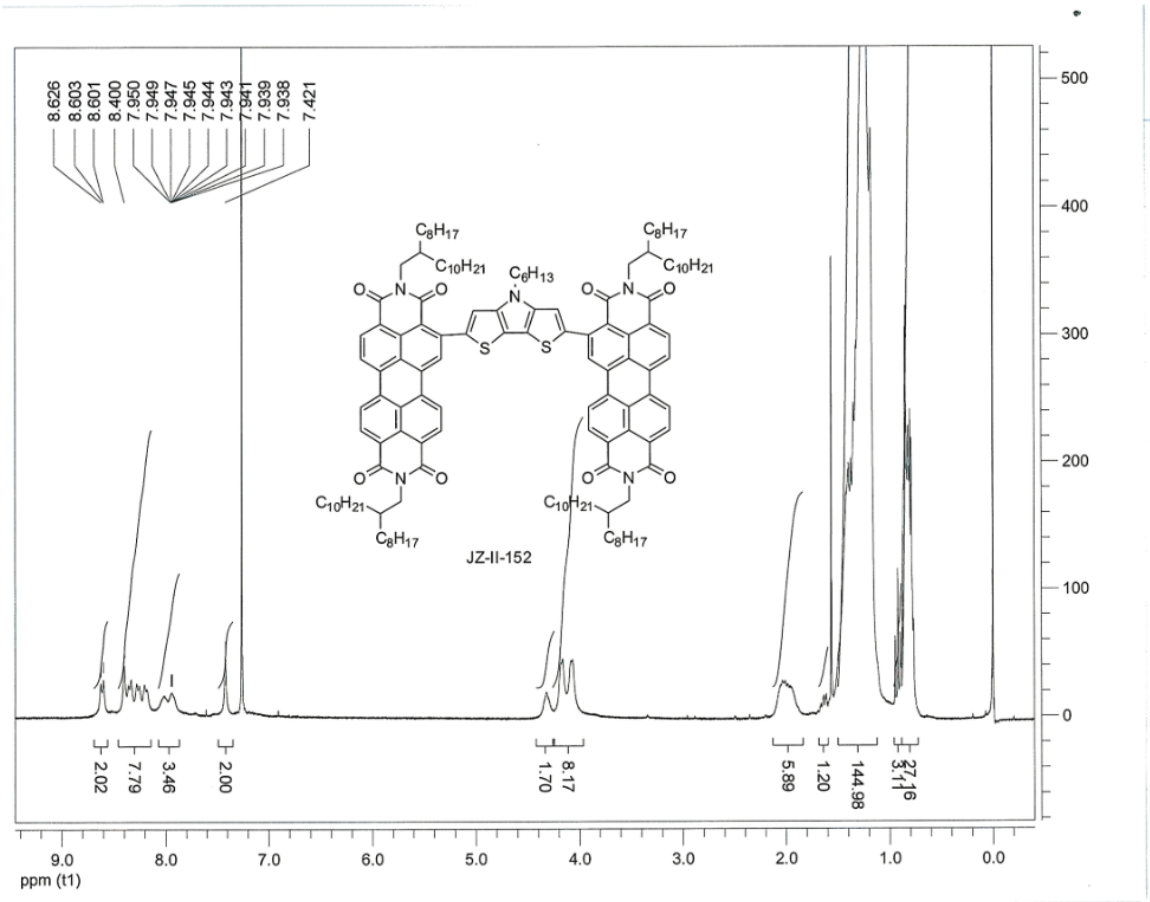
Compound **8**



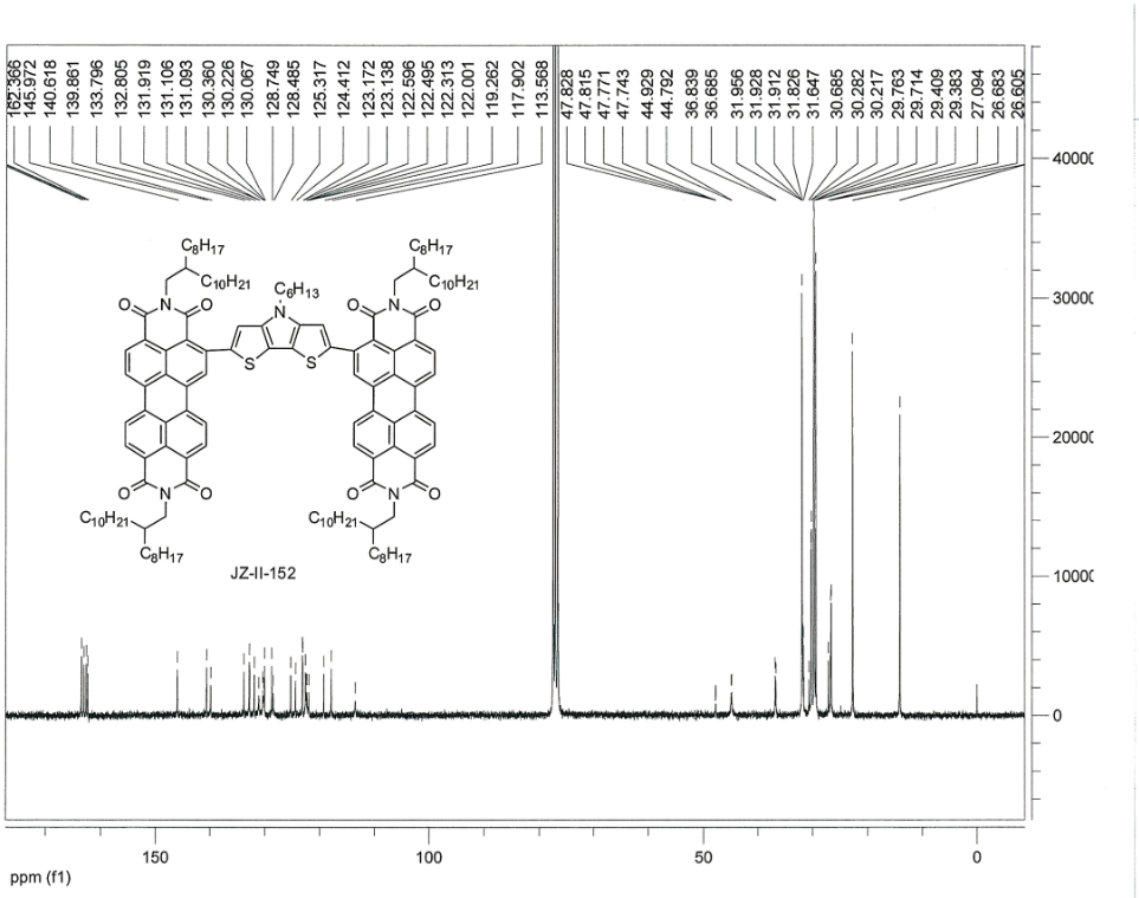
Compound **8**



Compound **9**



Compound **9**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128.485
125.317
124.412
123.172
123.138
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122.495
122.313
122.001
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113.568
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47.815
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47.743
44.929
44.792
36.839
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30.685
30.282
30.217
29.763
29.714
29.409
29.383
27.094
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100
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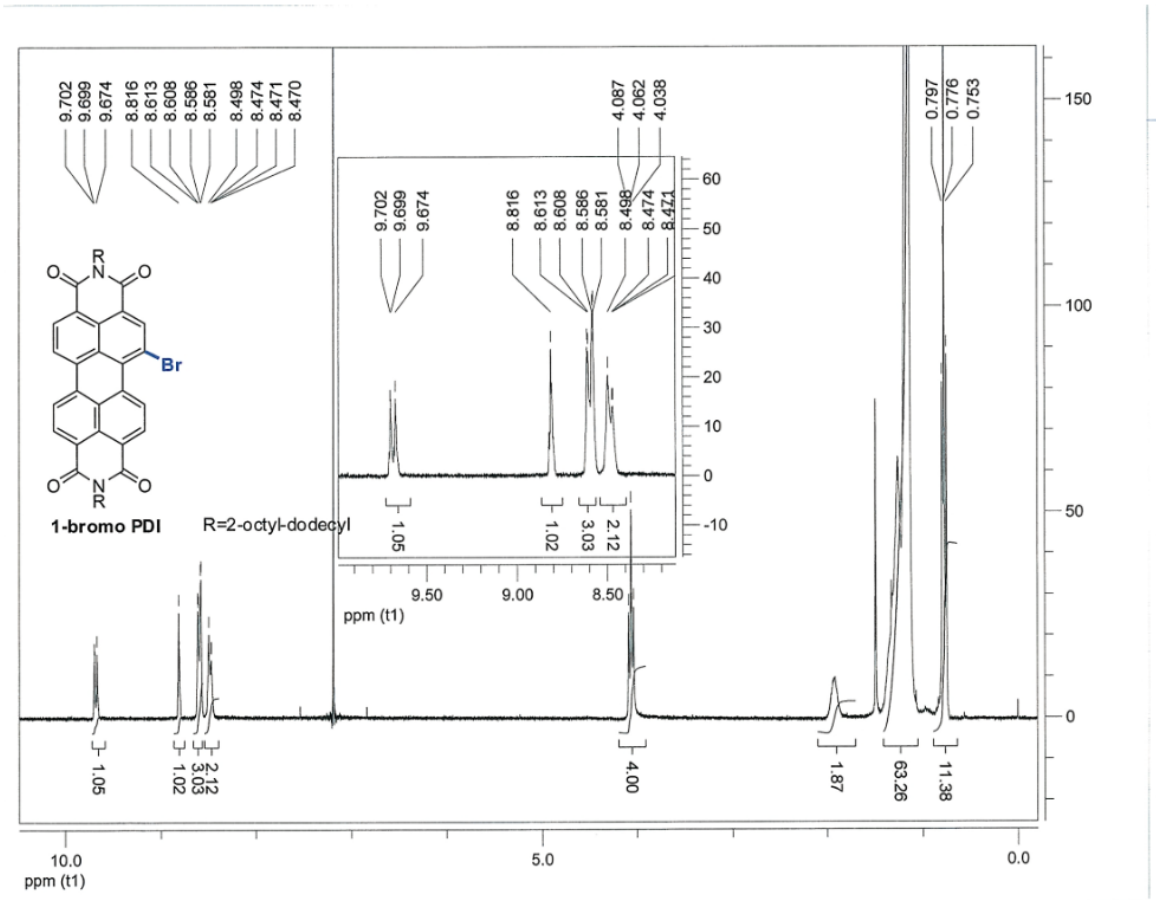
0
ppm (f1)

Compound **3**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9.699
9.674
8.816
8.613
8.608
8.586
8.581
8.498
8.474
8.471
8.470
4.087
4.062
4.038
0.797
0.776
0.753
Br
1-bromo PDI
R=2-octyl-dodecyl
1.05
1.02
3.03
2.12
4.00
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63.26
11.38
ppm (t1)
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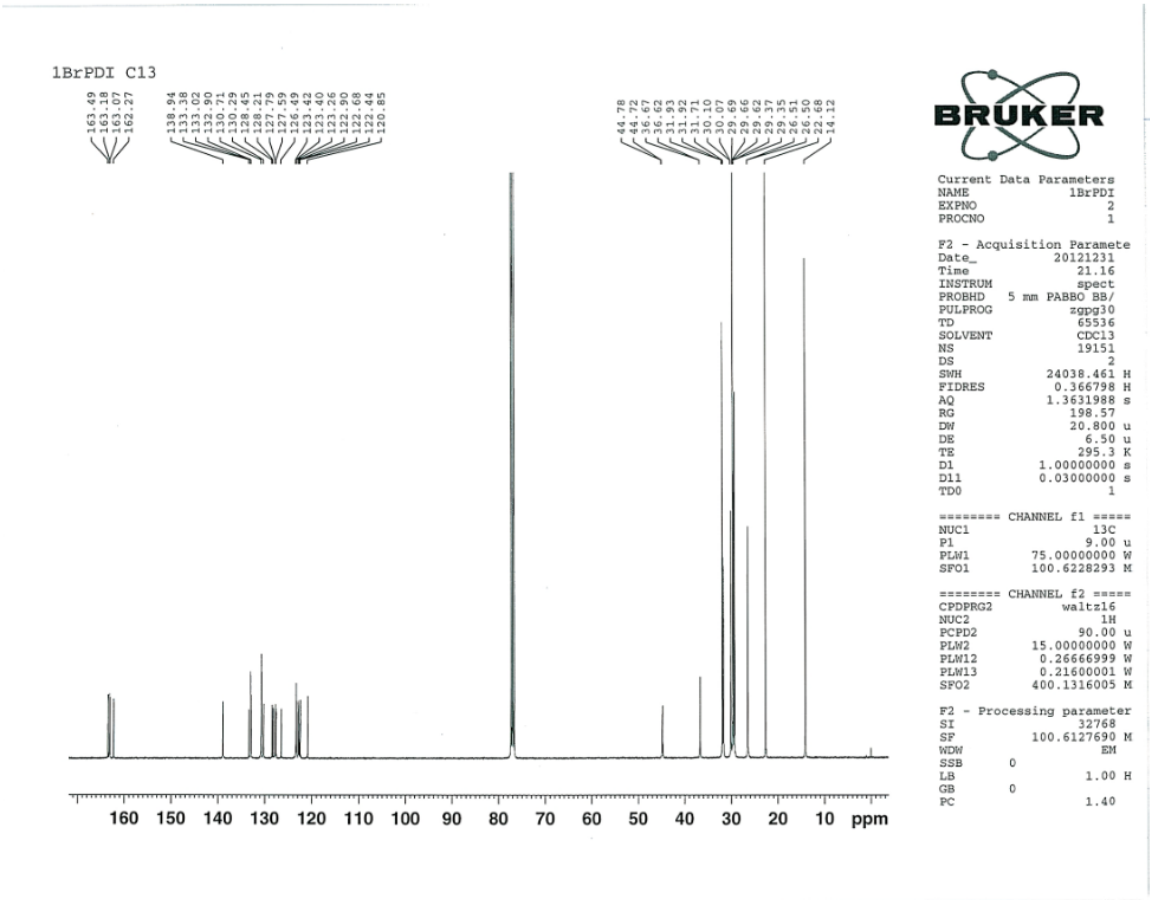
5.0
0.0
9.50
9.00
8.50

Compound **3**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163.07
162.27
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133.02
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128.21
127.79
127.59
127.49
125.42
123.40
123.26
122.90
122.68
122.44
120.85
44.78
44.72
36.67
36.63
31.93
31.92
31.71
30.10
30.07
29.69
29.66
29.62
29.37
29.35
26.51
26.50
22.68
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PCPD2 90.00 u
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PLW13 0.21600001 W
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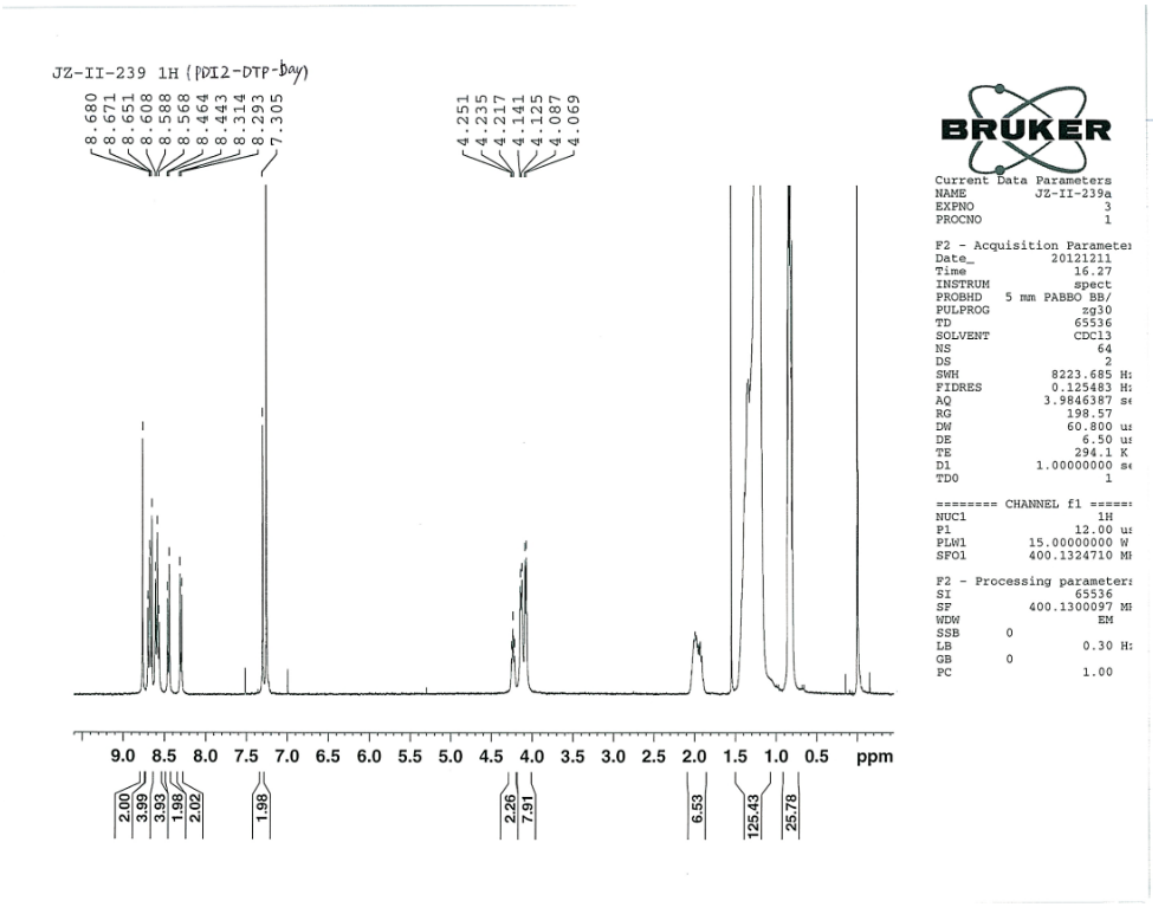
Compound **10**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8.651
8.608
8.588
8.568
8.464
8.443
8.314
8.293
7.305
4.251
4.235
4.217
4.141
4.125
4.087
4.069
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
3.99
3.93
1.98
2.02
1.98
2.26
7.91
6.53
125.43
25.78
BRUKER
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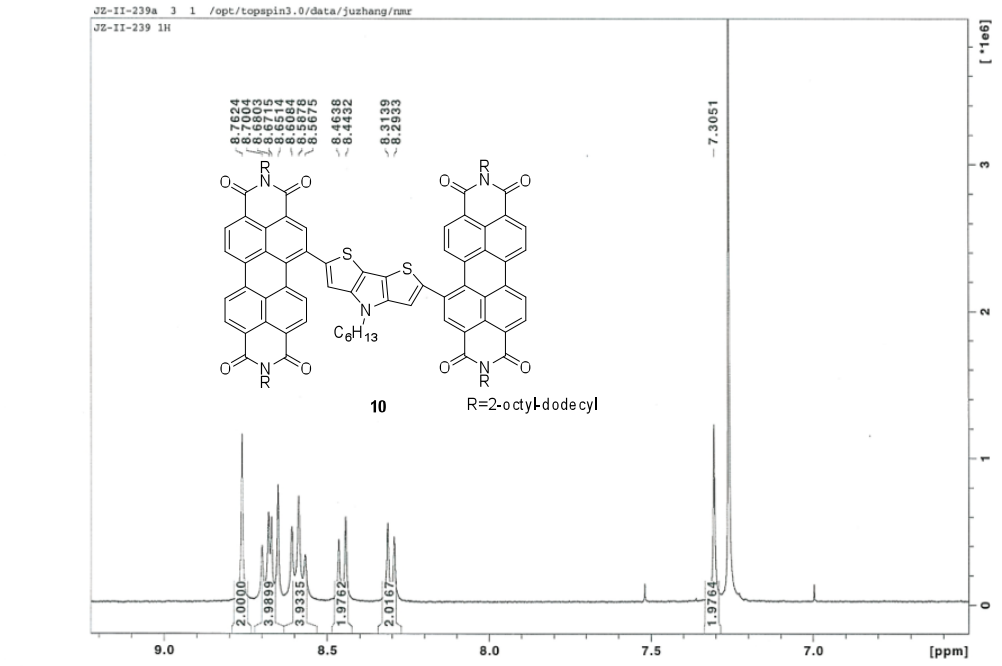
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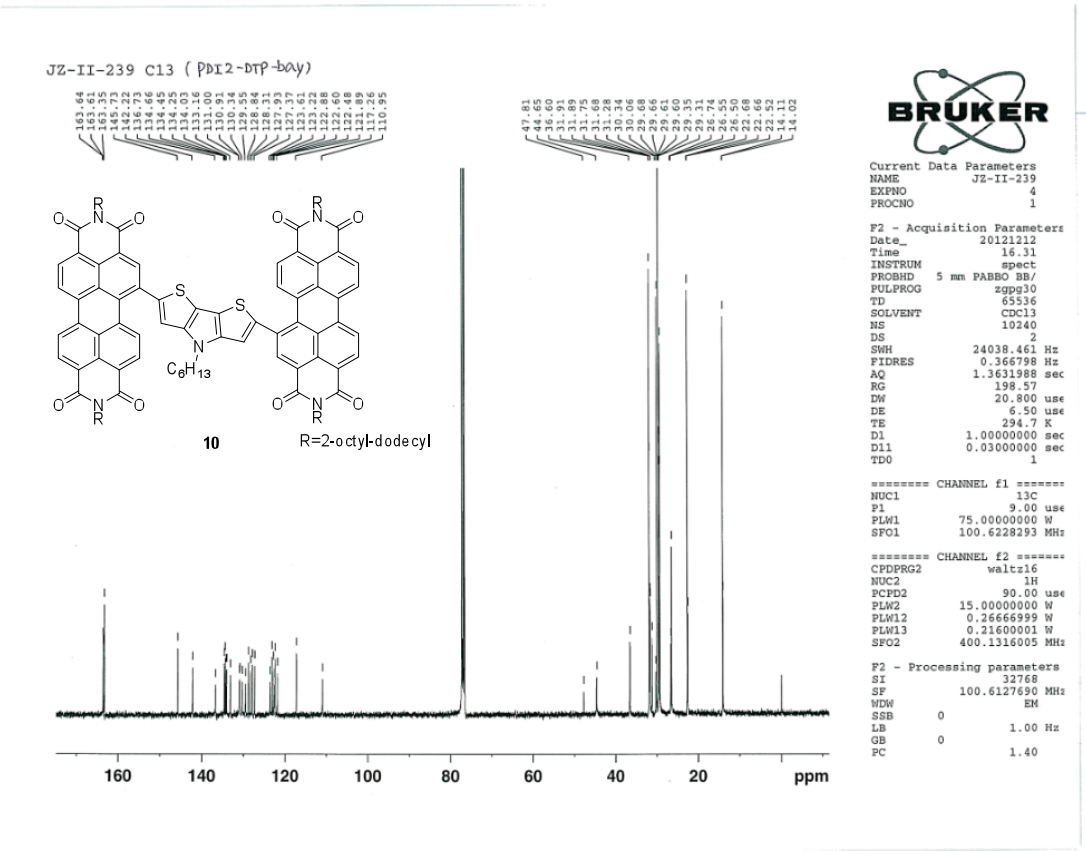
8.5878
8.5675
8.4638
8.4432
8.3139
8.2933
7.3051
2.000
3.989
3.935
1.976
2.016
1.976
9.0
8.5
8.0
7.5
7.0
[ppm]
[*1e6]
C6H13
10
R=2-octyl-dodecyl

Compound **10**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R=2-octyl-dodecyl
160
140
120
100
80
60
40
20
ppm
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LB 1.00 Hz
GB 0
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