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SUPPLEMENTARY INFORMATION

Comparing the microstructure and photovoltaic performance of 3 perylene imide acceptors with similar energy levels but different packing tendencies

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CONTENTS

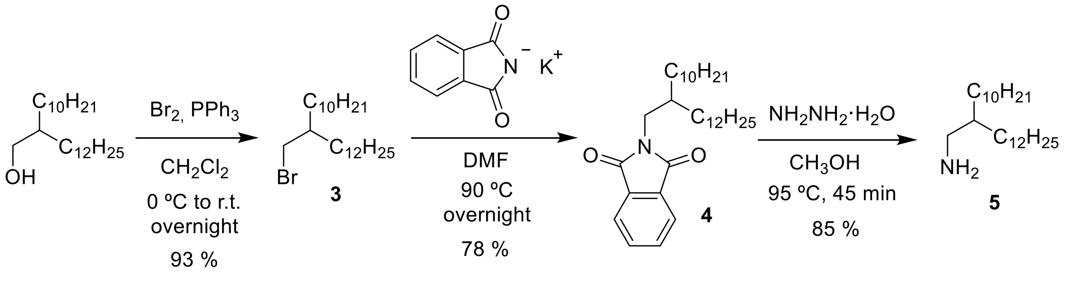
GENERAL EXPERIMENTAL DETAILS

All reagents were purchased from commercial suppliers and used without further purification. Polyamines **1** and **2** were obtained as previously described.[1,2] Solvents were dried distillation over sodium or benzophenone under argon before use. TLC analyses were performed using silica gel (Kieselgel 60 F254, Macherey–Nagel) and spots were visualized under UV light. Column chromatography was carried out with silica gel 60 (0.04-0.06 mm, Scharlau) columns, using the eluent reported in each case.

IR spectra are reported in wavenumbers (cm^{-1}). ^1H and ^{13}C NMR spectra were recorded using Bruker DPX 300MHz or Bruker AVIIII 300MHz BACS-60 systems at room temperature. Chemical shifts are given in ppm (δ) and referenced to the residual nondeuterated solvent frequencies ($CDCl_3$: δ 7.26 ppm for ^1H, δ 77 ppm for ^{13}C). Coupling constants (*J*) are in Hertz [Hz] and signals are described as follows: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad; app, apparent. High resolution mass spectra were recorded using MALDI-TOF techniques. UV–vis absorption spectra of the compounds in HPLC chloroform solutions at 20 °C were recorded on a Varian Cary 50 UV–vis spectrophotometer. Cyclic voltammetry experiments were performed with a computed controlled potentiostat in a three-electrode single-compartment cell (5 mL). The platinum working electrode consisted of a platinum wire with a surface of A = 0.785 mm^2, which was polished down to 0.5 μm with polishing paste prior to use in order to obtain reproducible surfaces. The counter electrode consisted of a platinum wire, and the reference electrode was a Ag/AgCl secondary electrode. An electrolyte solution of 0.1 M $TBAPF_6$ in freshly distilled and degassed CH_2Cl_2 (HPLC) was used in all experiments.

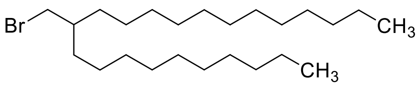
SYNTHETICAL PROCEDURES

SYNTHESIS OF 2-DECYL-1-TETRADECYLAMINE (5)[3]



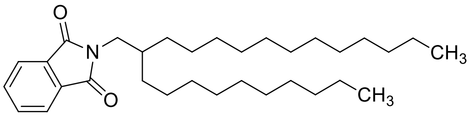
Scheme S1. Synthesis of **2-decyl-1-tetradecylamine 5**

2-Decyl-1-tetradecylbromide (3)



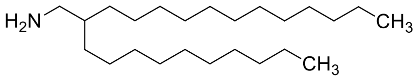
To a solution of triphenylphosphine (3.33 g, 12.7 mmol) in CH_2Cl_2 (20 mL) under argon atmosphere and cooled at 0 °C, bromine (0.65 mL, 12.7 mmol) was added dropwise. Then, 2-decyl-1-tetradecanol (5.35 mL, 12.7 mmol) was added dropwise and the mixture was allowed to react at room temperature overnight under argon. Solvent was evaporated and the crude washed with hexane and filtered. The filtrate was concentrated under rotatory evaporation, obtaining 4.92 g (93 %) of product **3** as colourless oil. Experimental data were consistent with previously reported literature values. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.43 (2H, d, *J* = 4.7 Hz, N-C*H*$_2$), 1.57 (1H, m, C*H*), 1.24 (40H, m, 20 C*H*$_2$), 0.86 (6H, m, 2 C*H*$_3$). This product was employed in the next step without further purification.

N-(2-Decyltetradecyl)phthalimide (4)



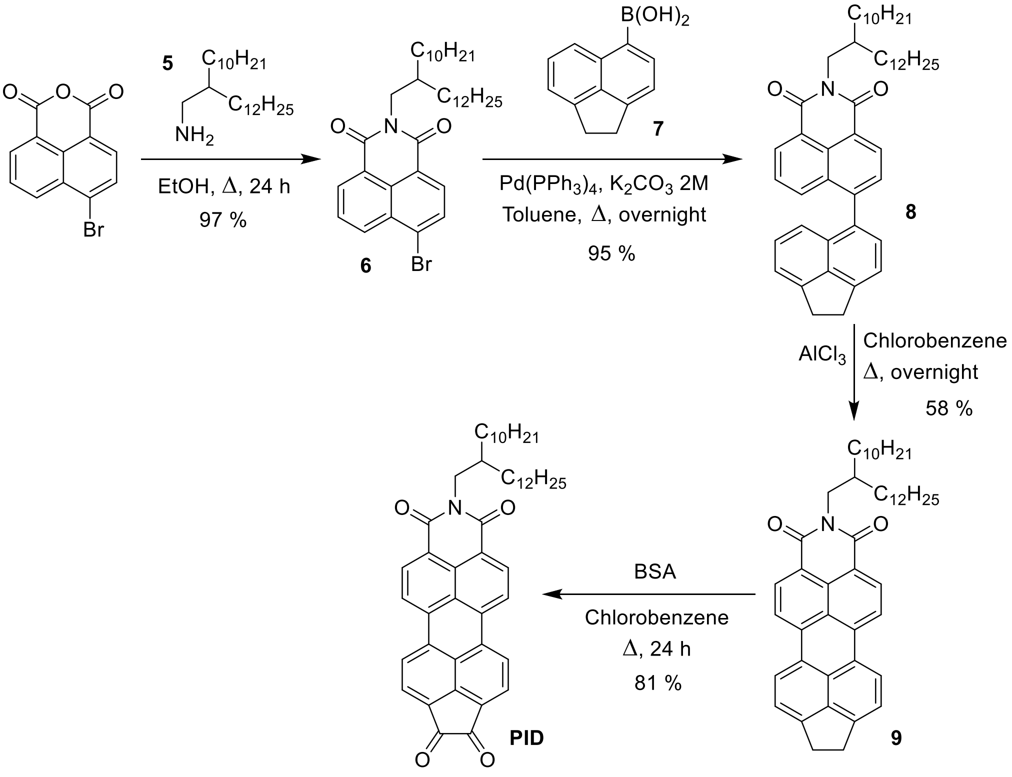
Potassium phthalimide (2.34 g, 12.6 mmol) was added to a solution of 2-decyl-1-tetradecylbromide **3** (4.90 g, 11.7 mmol) in 14 mL of dry DMF under argon and the reaction was stirred at 90 °C overnight. After cooling to room temperature, the reaction mixture was poured into 40 mL of water and extracted with dichloromethane (3 x 30 mL). The combined organic layers were washed with 100 mL of 0.2 M KOH, water, saturated NH_4Cl, dried over $MgSO_4$ and concentrated under reduced pressure. The resulting crude was purified by flash column chromatography (SiO_2, CH_2Cl_2) to give 4.34 g (78 %) of product **4** as a pale yellow oil. Experimental data were consistent with previously reported literature values. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.81 (2H, m, Ar*H*), 7.68 (2H, m, Ar*H*), 3.54 (2H, d, *J* = 7.2 Hz, N-C*H*$_2$), 1.84 (1H, m, C*H*), 1.49-1.29 (40H, m, 20 C*H*$_2$), 0.85 (6H, m, 2 C*H*$_3$).

2-Decyl-1-tetradecylamine (5)



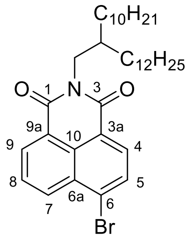
Hydrazine hydrate 51 % (1.28 mL) was added to a solution of *N*-(2-decyltetradecyl)phthalimide **4** (3.20 g, 6.6 mmol) in methanol (32 mL) and the mixture was stirred at 95 °C during 45 min. After cooling to room temperature, methanol was evaporated under reduced pressure. Dichloromethane (35 mL) was added to the residue and the resulting solution was washed with 10 % KOH (2 x 25 mL). Aqueous layers were combined and extracted with dichloromethane (3 x 10 mL). The combined organic layers were washed with brine (2 x 25 mL) and dried over $MgSO_4$. The evaporation of the solvent afforded the amine **5** as yellow oil (1.99 g, 85 % yield) which was used in the following step without further purification. Experimental data were consistent with previously reported literature values. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.44 (2H, br s, N*H*$_2$), 2.65 (2H, br d, *J* = 4.0 Hz, N-C*H*$_2$), 1.45 (1H, m, C*H*), 1.23 (40H, m, 20 C*H*$_2$), 0.85 (6H, m, 2 C*H*$_3$).

SYNTHESIS OF PID



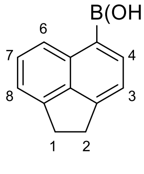
Scheme S2. Synthesis of **PID**

6-Bromo-2-(2-decyltetradecyl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (6)



A suspension of 4-bromo-1,8-naphthalicanhydride (930 mg, 3.35 mmol) in 33.5 mL of EtOH was refluxed. Then, 2-decyl-1-tetradecylamine **5** (1.95 g, 5.37 mmol) dissolved in 9.6 mL of EtOH was added dropwise and the mixture was heated for 24 h. The solvent was evaporated, and the product was purified by flash column chromatography (SiO_2, CH_2Cl_2) to give 1.99 g (97 %) of product **6** as an orange oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.65 (1H, dd, *J* = 7.3 and 0.9 Hz, *H*9), 8.56 (1H, dd, *J* = 8.5 and 0.9 Hz, *H*7), 8.41 (1H, d, *J* = 7.9 Hz, *H*4), 8.03 (1H, d, *J* = 7.9 Hz, *H*5), 7.84 (1H, dd, *J* = 8.5 and 7.3 Hz, *H*8), 4.10 (2H, d, *J* = 7.3 Hz, N-CH_2), 1.97 (1H, m, C*H*), 1.44-1.10 (40H, m, 20 CH_2), 0.87 (6H, m, 2 CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.6 (*C*1 or *C*3), 163.5 (*C*1 or *C*3), 137.7 (*C*7), 131.8 (*C*9), 131.0 and 130.8 (*C*4 and *C*5), 130.3 (*C*6a), 129.8 (*C*6), 128.7 (*C*10), 127.8 (*C*8), 123.0 (*C*9a), 122.1 (*C*3a), 44.5 (N-*C*H_2), 36.4 (*C*H), 31.8, 31.6, 29.9, 29.6, 29.5, 29.3, 29.2, 26.4 and 22.6 (overlapped signals, 20 *C*H_2), 14.0 (two overlapped signals, *C*H_3). FTIR (ATR, CH_2Cl_2): $\nu_{máx}$ = 3019, 2924, 2853, 1705, 1665, 1343, 1241, 748, 667. HRMS (EI) calculated for $C_{36}H_{54}{}^{79}BrNO_2$ [M$^{+\cdot}$] 611.3338, found 611.6342.

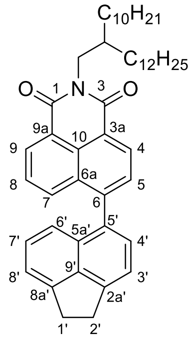
(1,2-Dihydroacenaphthylen-5-yl)boronic acid (7)[4]



To a solution of 5-bromo-1,2-dihydroacenaphthylene (400 mg, 1.72 mmol) in dry THF (5.2 mL), under argon atmosphere and cooled down at -78 °C,

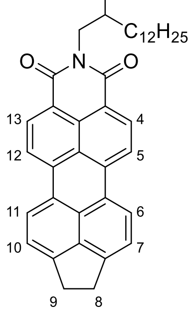
^{t}BuLi (2.24 mL, 3.8 mmol) was added dropwise during 2 h. After this time, triisopropyl borate (0.94 mL, 4.16 mmol) was added dropwise and the mixture was left to react at room temperature overnight. Then, 8 mL of HCl (10 %) was added to the reaction and it was extracted with ethyl acetate and dichlormethane. The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The resulting solid was treated with hexane and filtered, obtaining the desired product **7** as a beige solid (257.3 mg, 75 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.91 (1H, d, *J* = 8.4 Hz, *H*6), 8.66 (1H, d, *J* = 7.0 Hz, *H*4), 7.63 (1H, dd, *J* = 8.4 and 6.9 Hz, *H*7), 7.49 (1H, d, *J* = 7.0 Hz, *H*4), 7.40 (1H, d, *J* = 6.9 Hz, *H*8), 3.48 (4H, app s, *H*1 and *H*2), 1.54 (2H, br s, O*H*). FTIR (ATR, CH2Cl2): $\nu_{\text{máx}}$ = 3030, 2923, 1602, 1496, 1405, 1350, 1318, 1237, 1108, 1078, 840, 774, 721, 620.

2-(2-Decyltetradecyl)-6-(1,2-dihydroacenaphthylen-5-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (8)



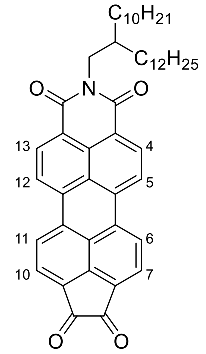
To a degassed solution of imide **6** (1.16 g, 1.9 mmol) and acenaphthene-5-boronic acid **7** (0.376 g, 1.9 mmol) in 25 mL of toluene was added 9.5 mL of a degassed solution of K_2CO_3 (2 M) and $Pd(PPh_3)_4$ (84.3 mg, 0.127 mmol) under argon. The mixture was refluxed overnight. Then, the solvent was evaporated, and the mixture was dissolved in DCM, washed with water, and dried over anhydrous $MgSO_4$. The product was purified (SiO_2, hexane/CH_2Cl_2 7:3) to give the desired compound **8** (1.24 g, 95 %) as yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.70 (1H, d, *J* = 7.4 Hz, *H*4), 8.61 (1H, dd, *J* = 7.2 and 1.1 Hz, *H*9), 7.94 (1H, dd, *J* = 8.5 and 1.1 Hz, *H*7), 7.80 (1H, d, *J* = 7.5 Hz, *H*5), 7.57 (1H, dd, *J* = 8.5 and 7.4 Hz, *H*8), 7.49 (1H, d, *J* = 7.0 Hz, *H*4'), 7.46 (1H, d, *J* = 7.0 Hz, *H*3'), 7.34 (2H, m, *H*6' and *H*8'), 7.10 (1H, app t, *J* = 4.6 Hz, *H*7'), 4.17 (2H, d, *J* = 7.3 Hz, N-C*H*₂), 3.52 (4H, app s, *H*1' and *H*2'), 2.05 (1H, m, C*H*), 1.45-1.25 (40H, m, 20 C*H*₂), 0.90 (6H, m, 2 C*H*₃). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.7 (*C*1 or *C*3), 164.6 (*C*1 or *C*3), 147.1 (*C*2a'), 146.3 (*C8*a'), 145.2 (*C*6), 139.3 (*C*9'), 132.9 (*C*7), 131.8, 131.1, 130.6 and 128.6 (*C*6a, *C*10, *C*5' and *C*5a'), 131.2 (*C*9), 130.9 (*C*4), 129.7 (*C*4'), 128.9 (*C*5), 128.5 (*C*6' or *C*8'), 126.6 (*C*8), 122.9 (*C*9a), 122.0 (*C*3a), 120.7 (*C*7'), 119.8 (*C*8' or *C*6'), 118.9 (*C*3'), 44.6 (N-CH_2), 36.7 (*C*H), 31.9, 31.7, 30.6, 30.3, 30.1, 29.7, 29.4, 26.4 and 22.7 (overlapped signals, *C*1', *C*2' and 20 *C*H_2), 14.1 (two overlapped signals, *C*H_3). FTIR (ATR, CH_2Cl_2): $\nu_{\text{máx}}$ = 2924, 2853, 1702, 1662, 1590, 1510, 1460, 1351, 1234, 1178, 1073, 837, 782. HRMS (MALDI-TOF) calculated for $C_{48}H_{63}NO_2$ [M^+] 686.4859, found $[M+H]^+$ 686.4917.

2-(2-Decyltetradecyl)-8,9-dihydro-1*H*-indeno[6',7',1':10,5,6]anthra[2,1,9-*def*]isoquinoline-1,3(2*H*)-dione (9)



To a solution of 460 mg (3.4 mmol) of $AlCl_3$ in 15 mL of anhydrous chlorobenzene under argon atmosphere, imide **8** (233.2 mg, 0.34 mmol) was added and the mixture was refluxed during 5 hours. Then, the mixture was cooled to room temperature and water was added. The mixture was extracted and dried over $MgSO_4$, and the solvent was evaporated. The red solid was purified by chromatography (SiO_2, hexane/CH_2Cl_2 1:1) to give compound **9** as a dark red solid (134.9 mg, 58 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.39 (2H, d, *J* = 8.0 Hz, *H*4(13)), 8.12 (2H, d, *J* = 7.5 Hz, *H*6(11)), 8.07 (2H, d, *J* = 8.0 Hz, *H*5(12)), 7.34 (2H, d, *J* = 7.5 Hz, *H*7(10)), 4.1 (2H, d, *J* = 7.3 Hz, N-CH_2), 3.42 (4H, s, *H*8(9)), 2.01 (1H, m, C*H*), 1.33-1.10 (40H, m, 20 CH_2), 0.84 (6H, m, 2 CH_3). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 164.1 (N-*C*O), 149.6 (*C*7a(9a), 138.3 (*C*17), 137.1 (*C*5a(11b)), 131.2 (*C*4(13)), 130.2 (*C*14), 129.0, 127.0, 125.7 and 120.0 (*C*3a(13a), *C*5b(11a), *C*15 and *C*16), 124.8 (*C*6(11)), 121.0 (*C*7(10)), 118.9 (*C*5(12)), 44.8 (N-*C*H$_2$), 36.6 (*C*H), 31.9, 31.0, 30.0, 29.7, 29.6, 29.3, 26.3, and 22.7 (overlapped signals, *C*8(9) and 20 *C*H$_2$), 14.1 (two overlapped signals, *C*H$_3$). Signals of quaternary carbons at 138.3, 129.0 and 127.0 ppm have been detected by HMBC. FTIR (ATR, CH$_2$Cl$_2$): $\nu_{\text{máx}}$ = 2924, 2853, 1702, 1662, 1590, 1510, 1460, 1351, 1234, 1178, 1073, 837, 782. HRMS (MALDI-TOF) calculated for $C_{48}H_{62}NO_2$ [M$^+$] 683.4702, found [M+H]$^+$ 684.4763.

2-(2-Decyltetradecyl)-1*H*-indeno[6',7',1':10,5,6]anthra[2,1,9-*def*]isoquinoline-1,3,8,9(2*H*)-tetraone (PID)



To a solution of 357 mg (0.52 mmol) of imide **9** in 55 mL of anhydrous chlorobenzene under argon atmosphere, benzeneseleninic acid anhydride (BSA, 1.72 mmol) was added and the mixture was refluxed during 24 h. Then, the mixture was cooled to room temperature and the solvent was removed under vacuum. The residue was dissolved in CH$_2$Cl$_2$ and washed with water. The organic layer was dried with MgSO$_4$, and the solvent was once again evaporated. The red solid was purified by chromatography (SiO$_2$, CH$_2$Cl$_2$) to give **PID** as a dark red solid (301 mg, 81 %). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.65 (2H, d, *J* = 8.0 Hz, *H*4(13)), 8.52 (4H, m, *H5*(12) and *H*6(11)), 8.13 (2H, d, *J* = 7.7 Hz, *H*7(10)), 4.12 (2H, d, *J* = 7.3 Hz, N-CH_2), 2.00 (1H, m, C*H*), 1.49-1.09 (40H, m, 20 CH_2), 0.85 (6H, m, 2 CH_3). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 185.8, 162.4, 153.7, 146.1, 134.1, 133.2, 130.4, 128.7, 127.9, 122.7, 122.4, 122.2, 121.6, 43.7, 30.9, 30.6, 29.0, 28.6, 28.3, 25.4, 21.6, 13.1 (some aliphatic signals overlap). FTIR (ATR, CH$_2$Cl$_2$): $\nu_{\text{máx}}$ = 2923, 2853, 1728, 1699, 1654, 1608, 1582, 1414, 1355, 1315, 1241, 1214, 1016, 808, 750, 6667. HRMS (MALDI-TOF) calculated for $C_{48}H_{58}NO_4$ [M+H $^+$] 712.4288, found 712.4388.

NMR SPECTRA

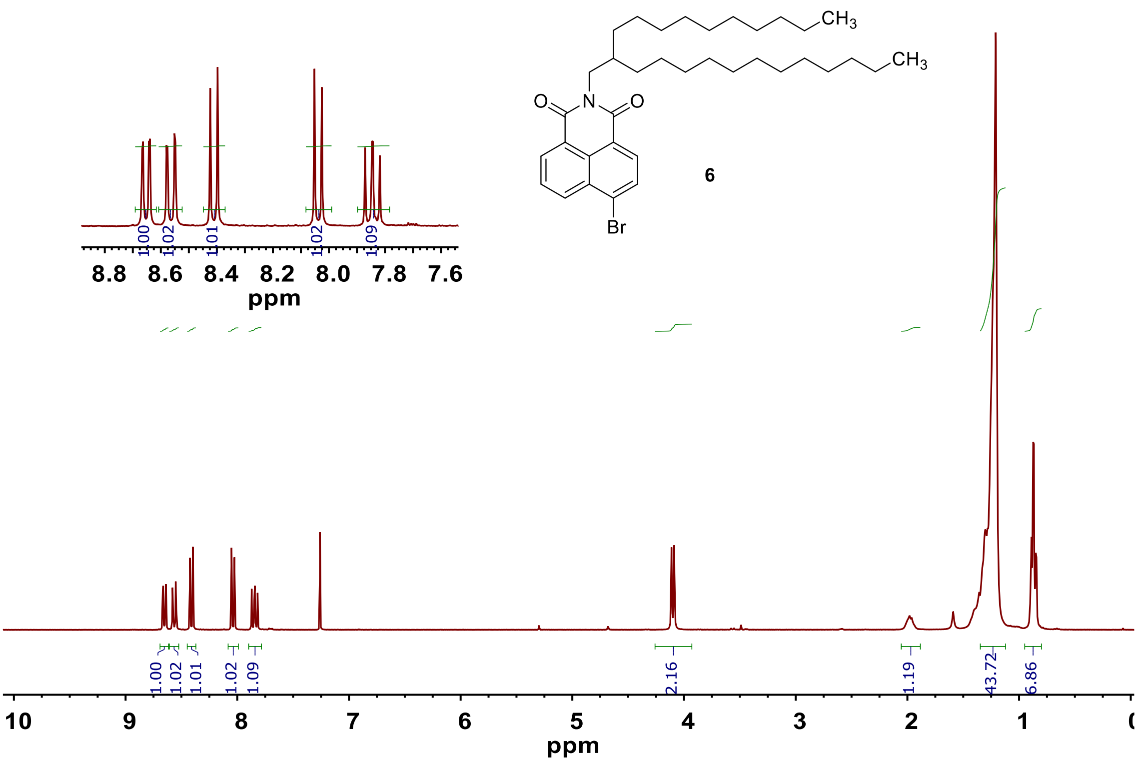


Figure S1. ^{1}H-NMR spectrum of **6** in $CDCl_3$.

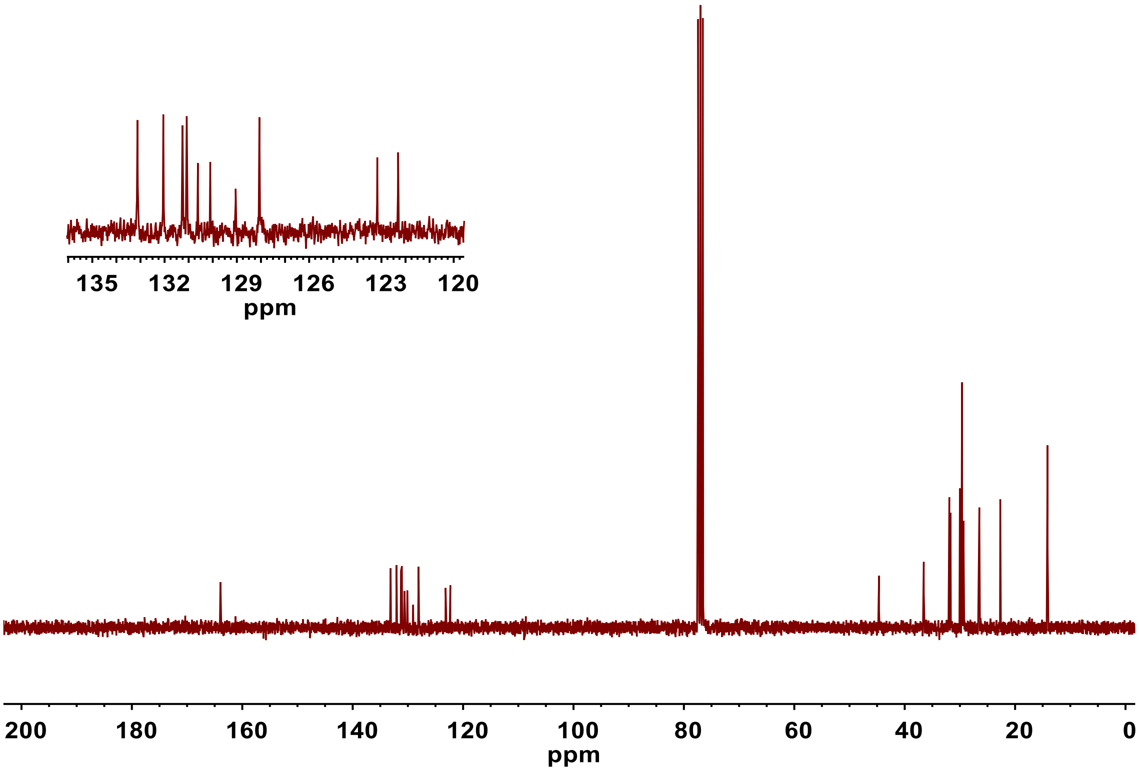


Figure S2. ^{13}C-NMR spectrum of **6** in $CDCl_3$.

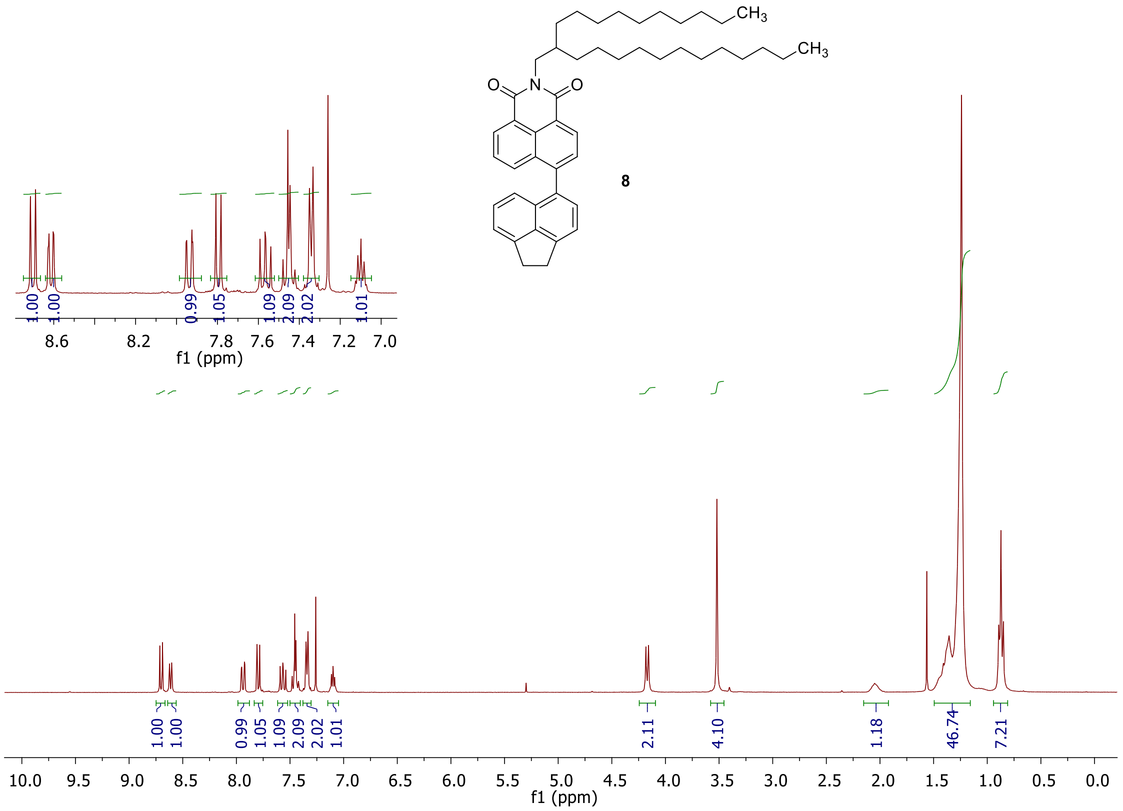


Figure S3. ^{1}H-NMR spectrum of **7** in $CDCl_3$.

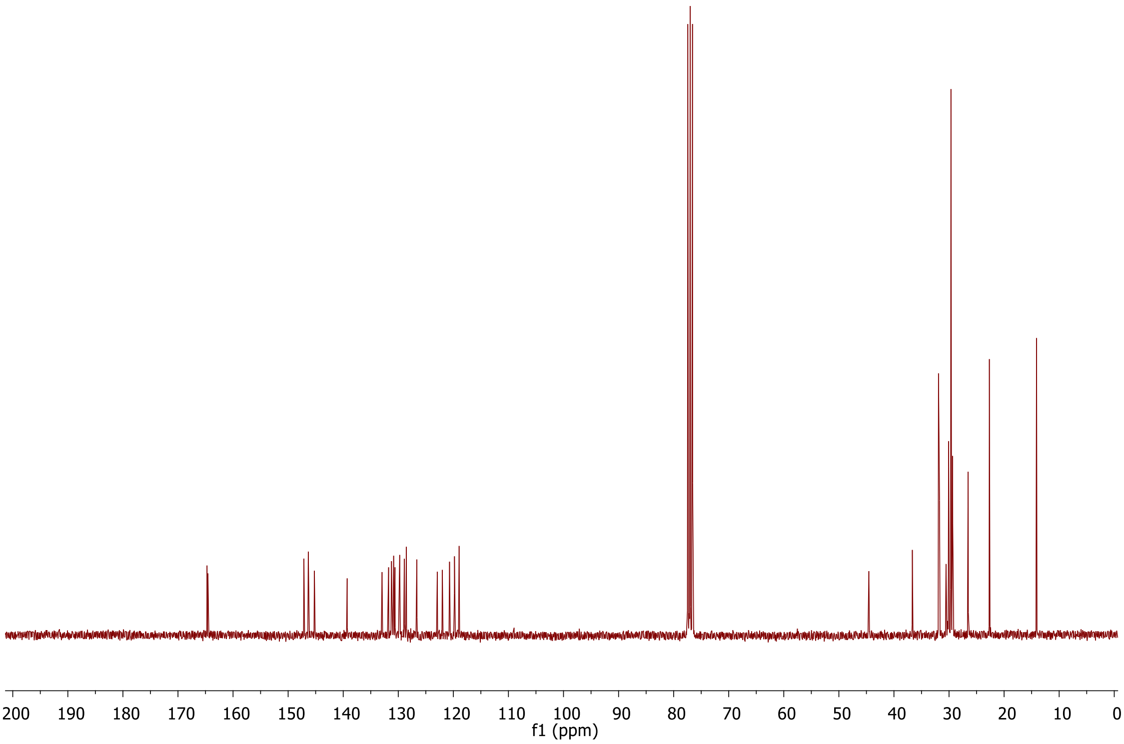


Figure S4. ^{13}C-NMR spectrum of **8** in $CDCl_3$.

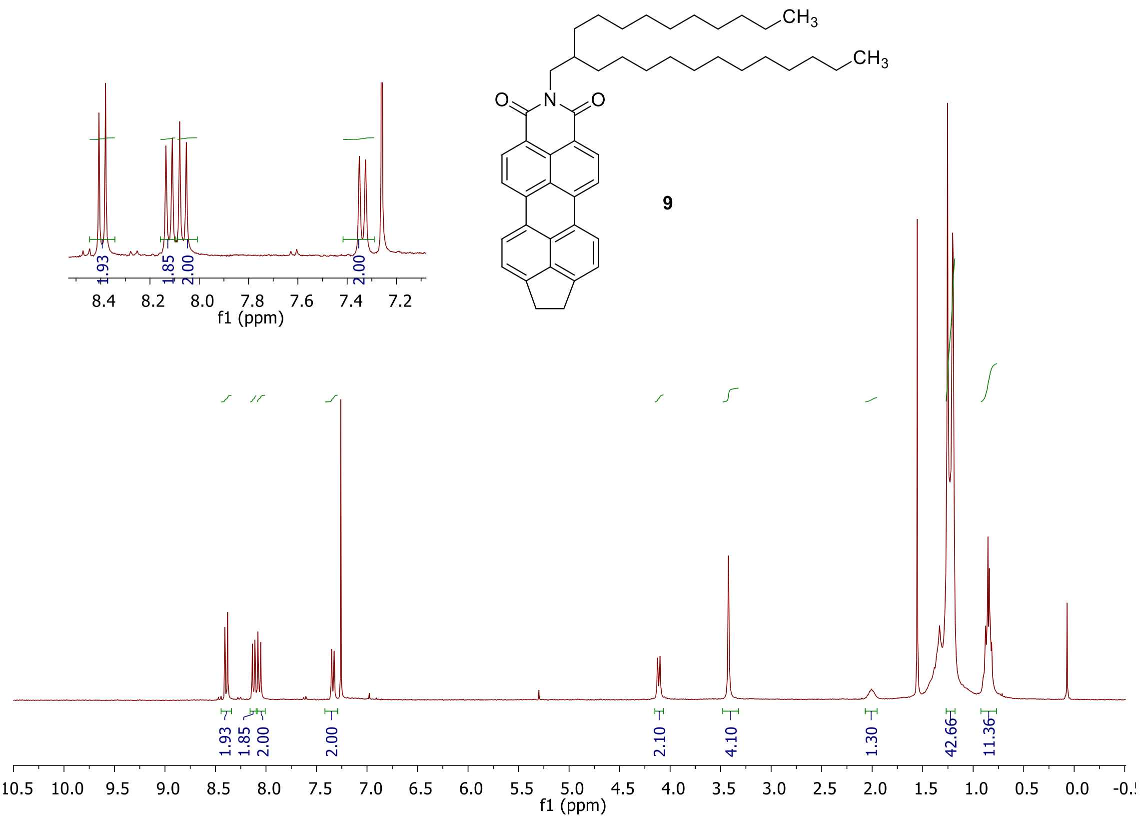


Figure S5. ^{1}H-NMR spectrum of **9** in $CDCl_3$.

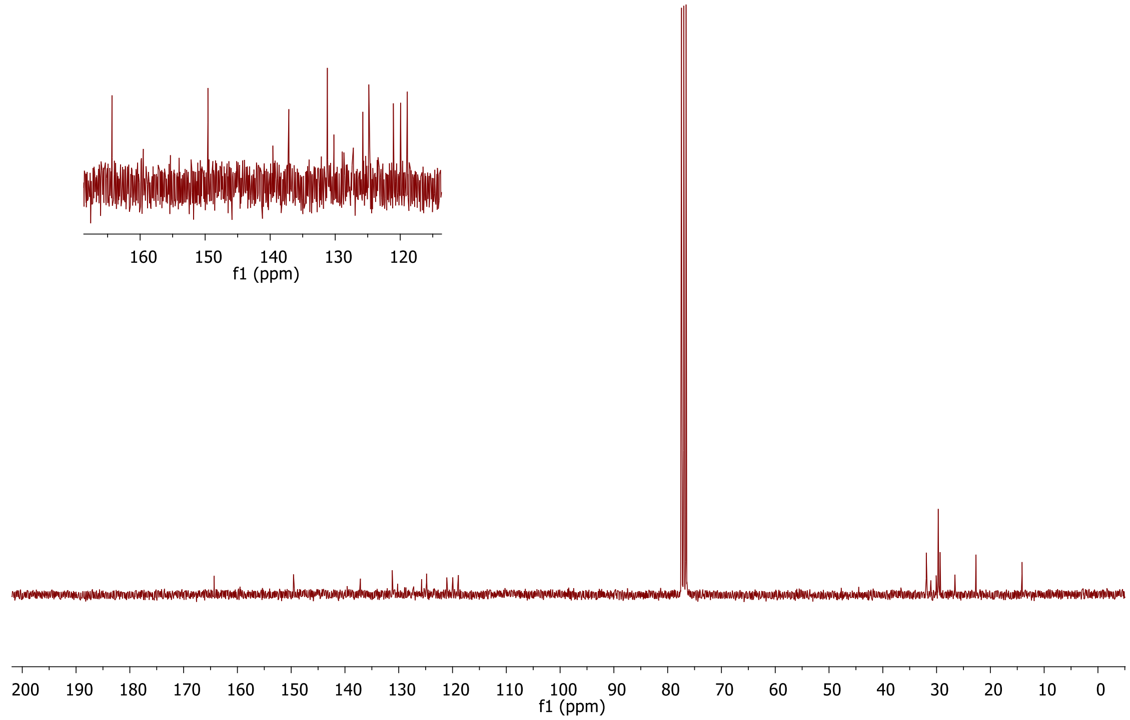


Figure S6. ^{13}C-NMR spectrum of **9** in $CDCl_3$.

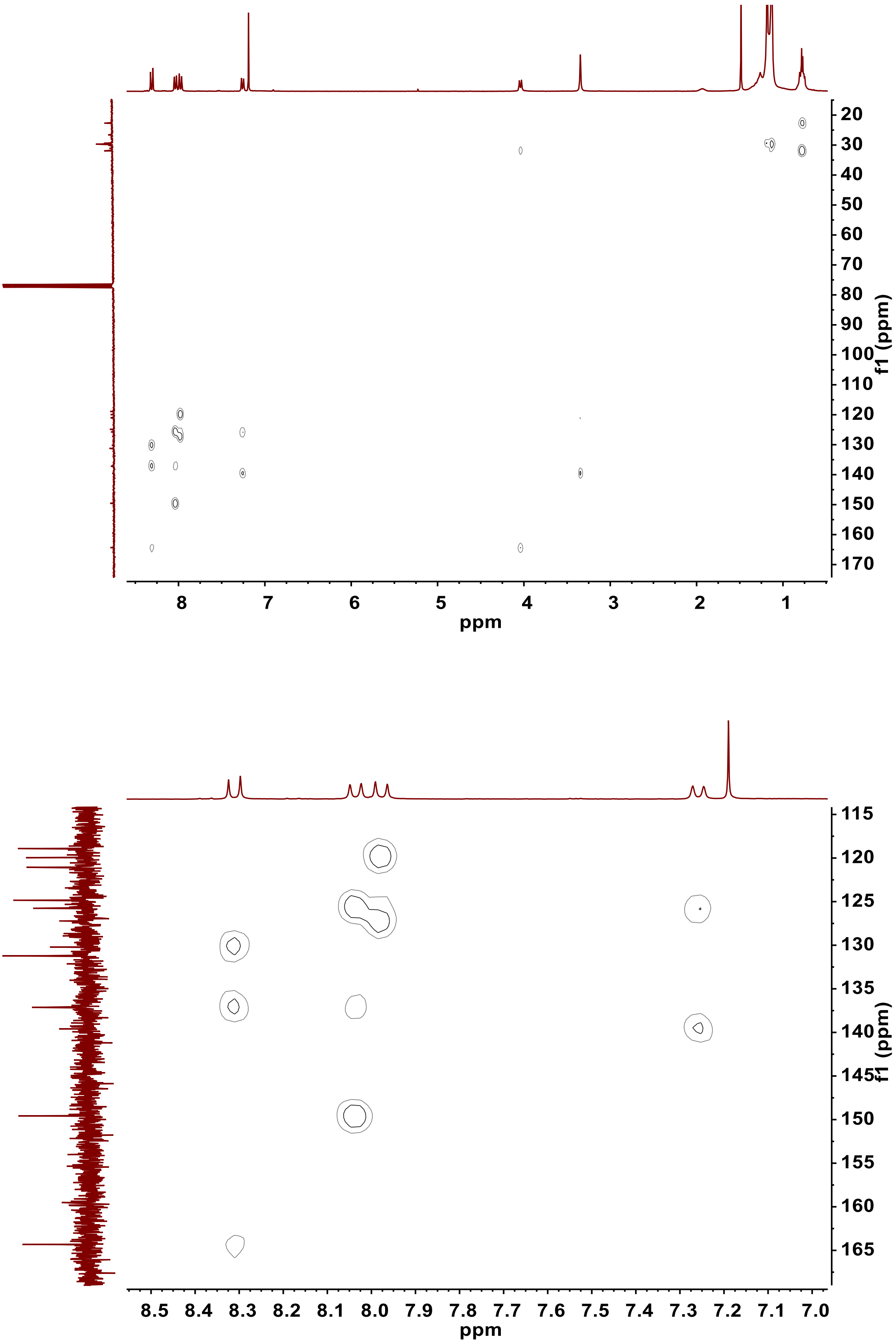


Figure S7. HMBC spectrum of **9** in $CDCl_3$ and its extention.

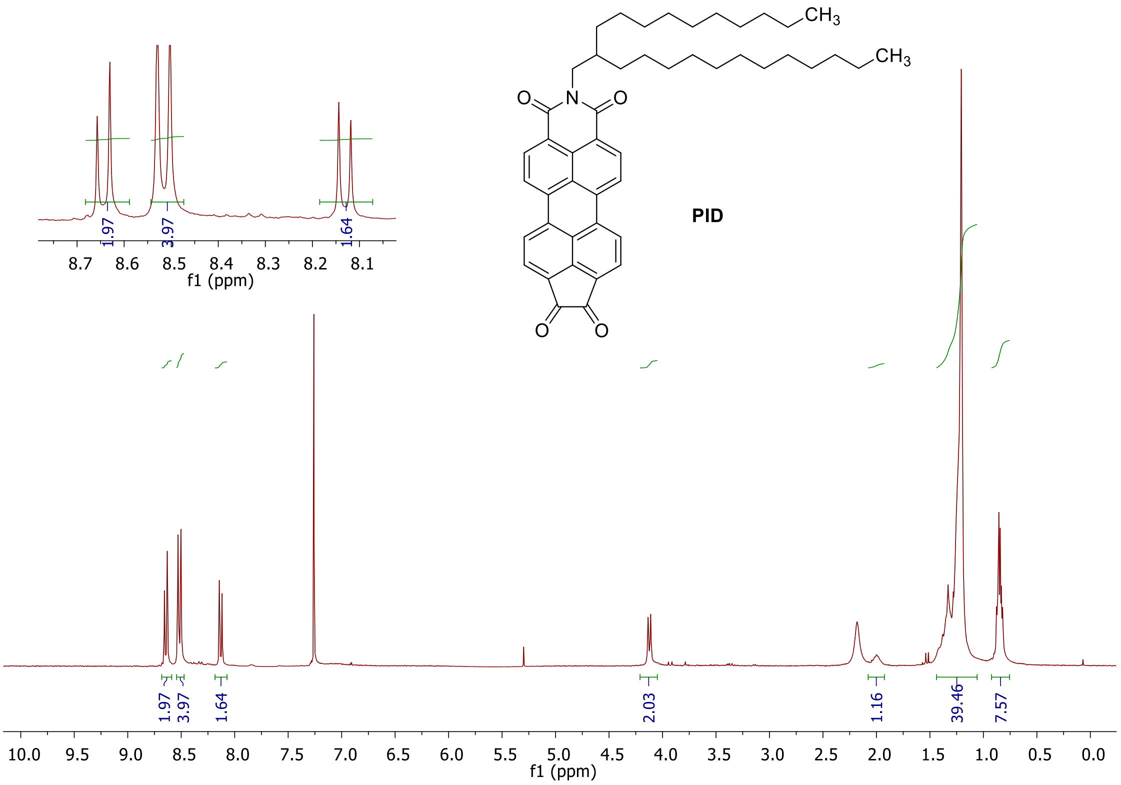


Figure S8. ^{1}H-NMR spectrum of **PID** in $CDCl_3$.

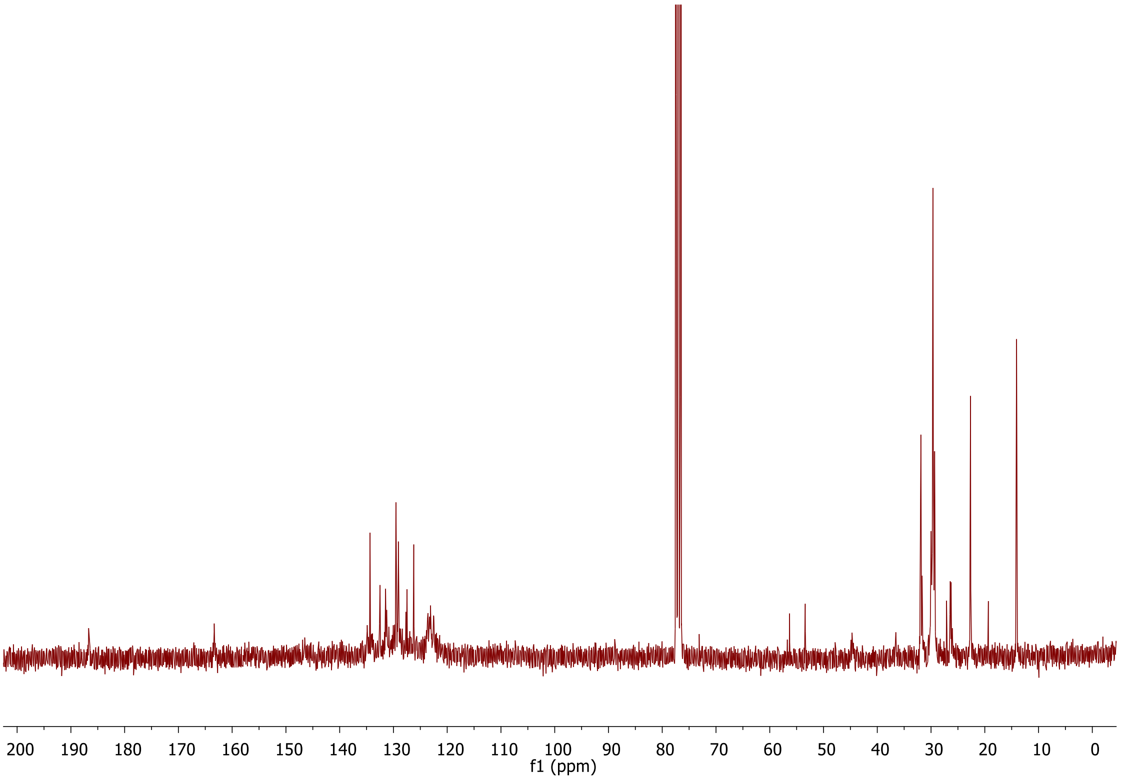


Figure S9. ^{13}C-NMR spectrum of **PID** in $CDCl_3$.

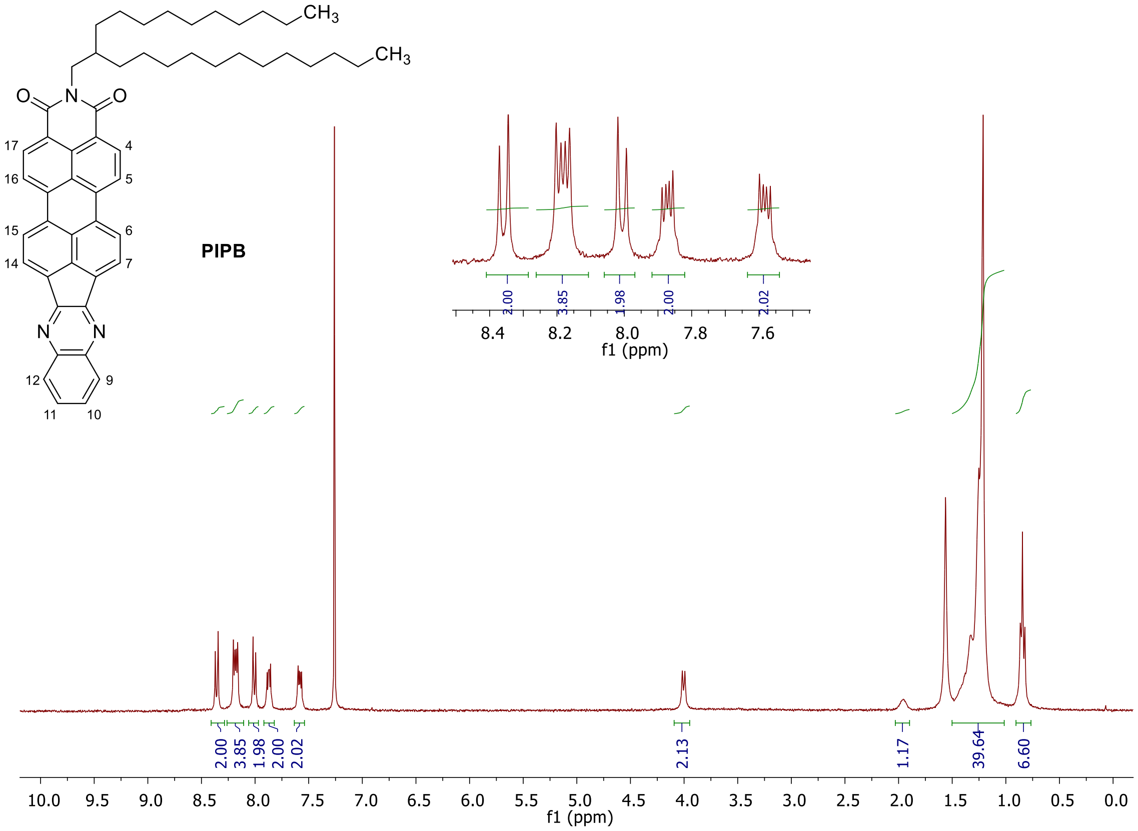


Figure S10. ^{1}H-NMR spectrum of **PIPB** in $CDCl_3$.

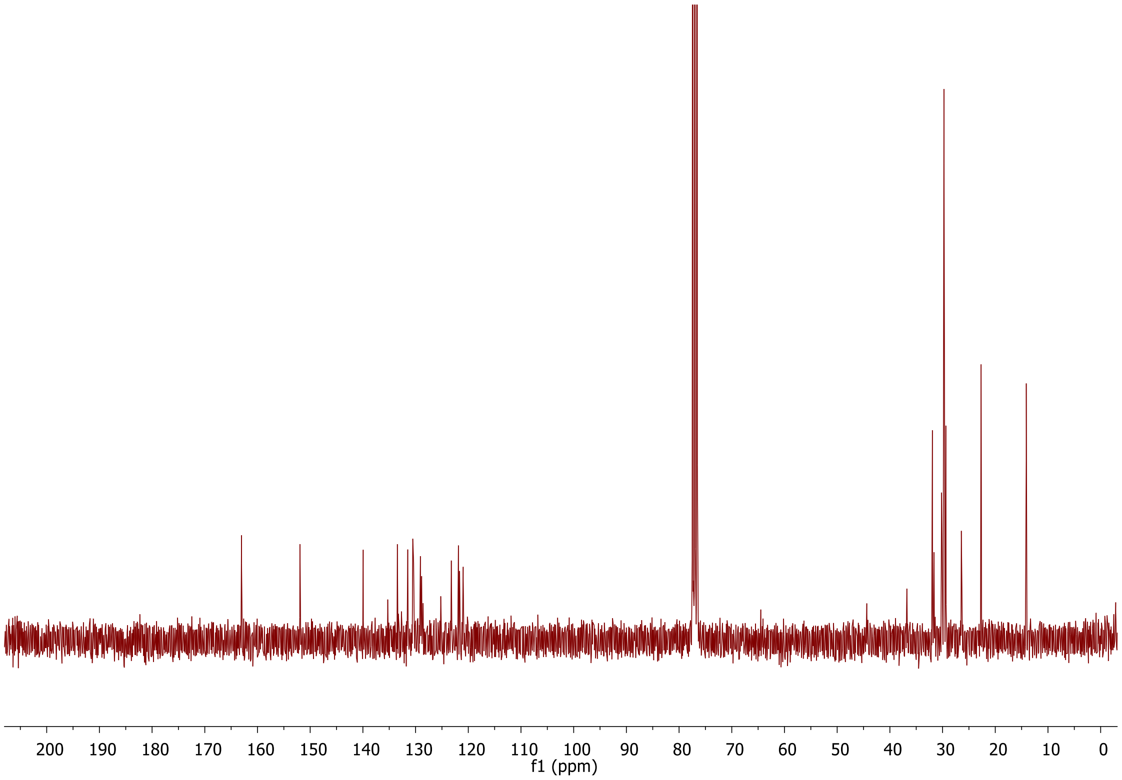


Figure S11. ^{13}C-NMR spectrum of **PIPB** in $CDCl_3$.

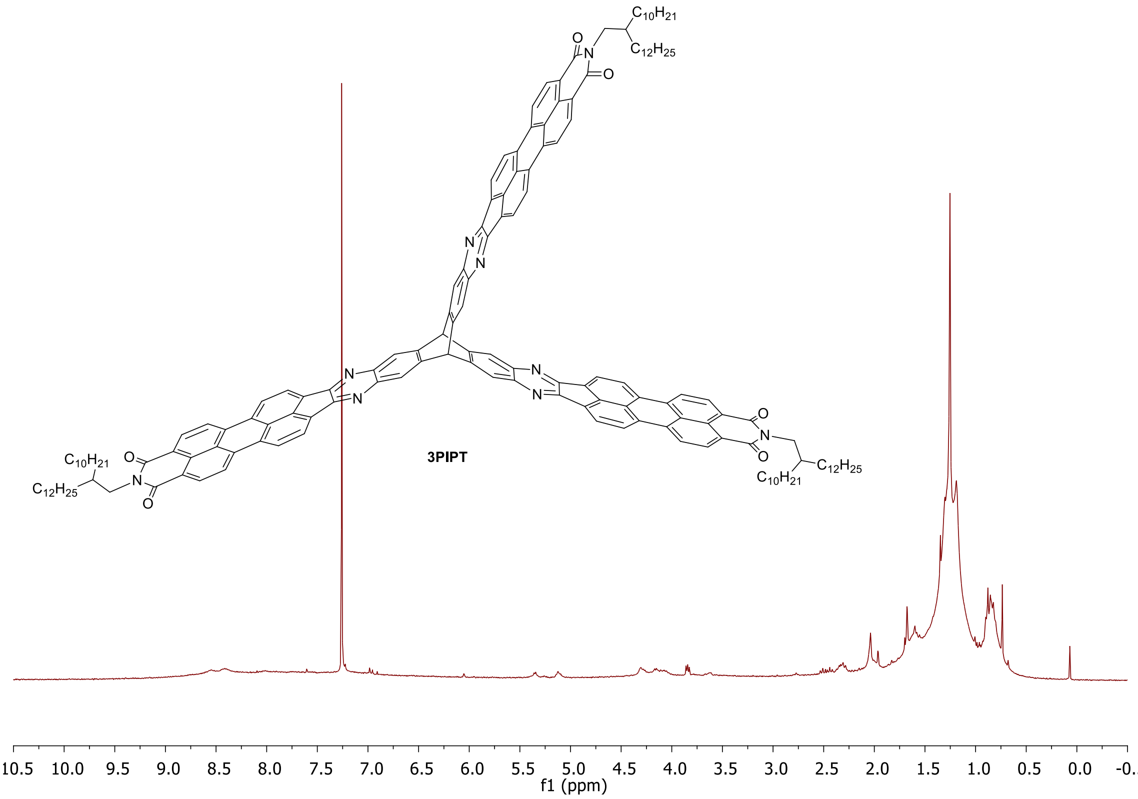


Figure S12. ^{1}H-NMR spectrum of **3PIPT** in $CDCl_3$.

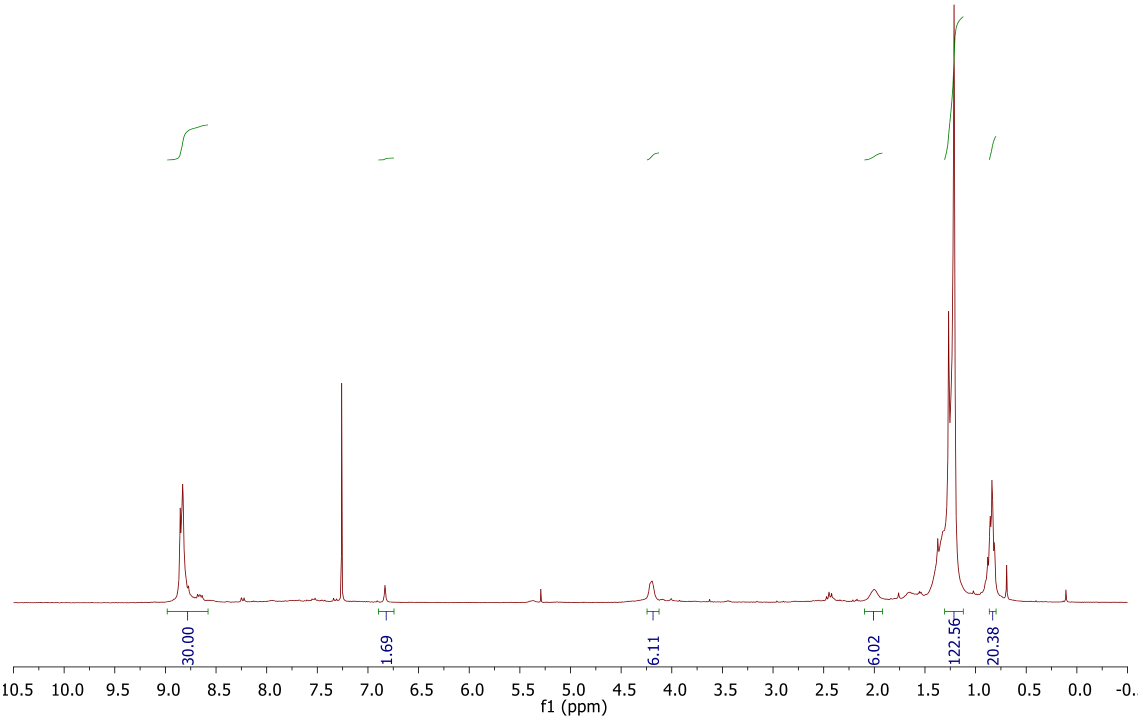


Figure S13. ^{1}H-NMR spectrum of **3PIPT** in $CDCl_3$ with TFA.

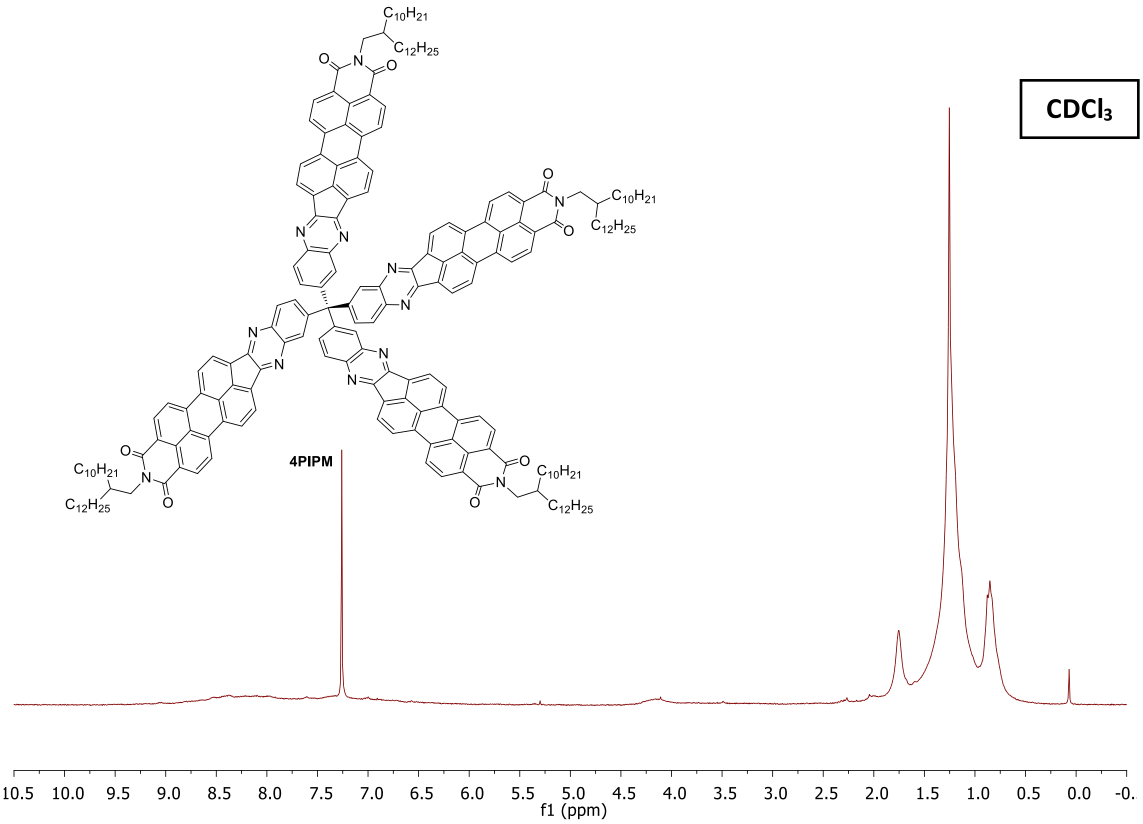


Figure S14. ^{1}H-NMR spectrum of **4PIPM** in $CDCl_3$.

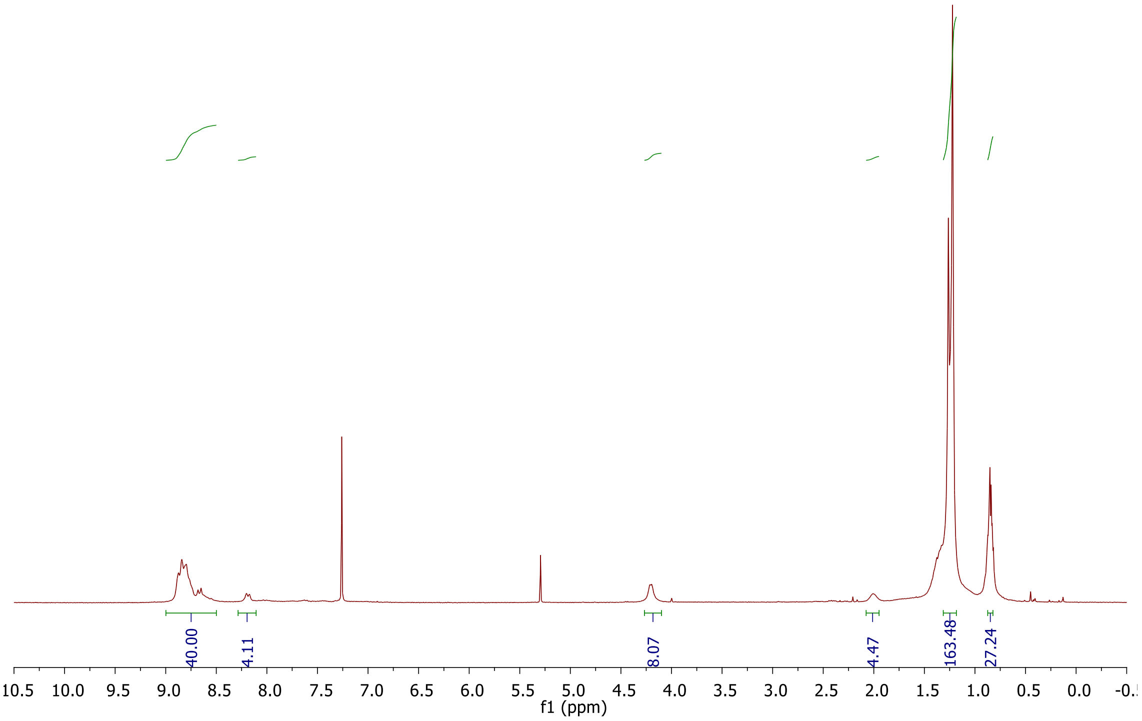
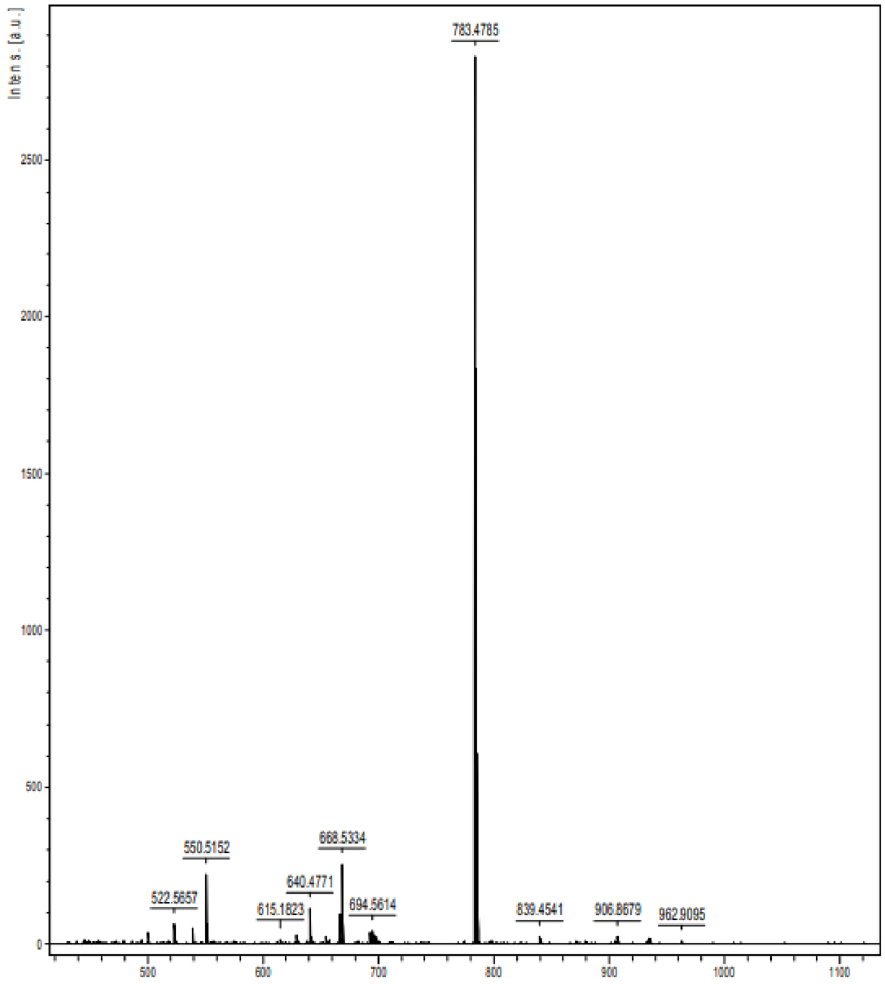
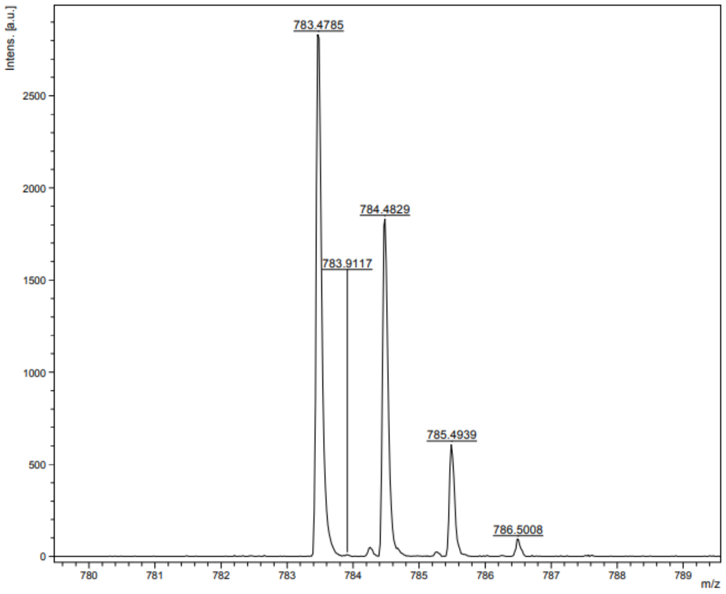
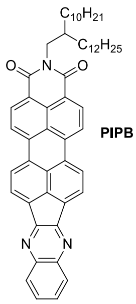


Figure S15. ^{1}H-NMR spectrum of **4PIPM** in $CDCl_3$ with TFA.

MASS SPECTRA OF PIPB, 3PIPT AND 4PIPM







PIPB

Figure S16. MALDI-HRMS (m/z) mass spectrum of **PIPB**.

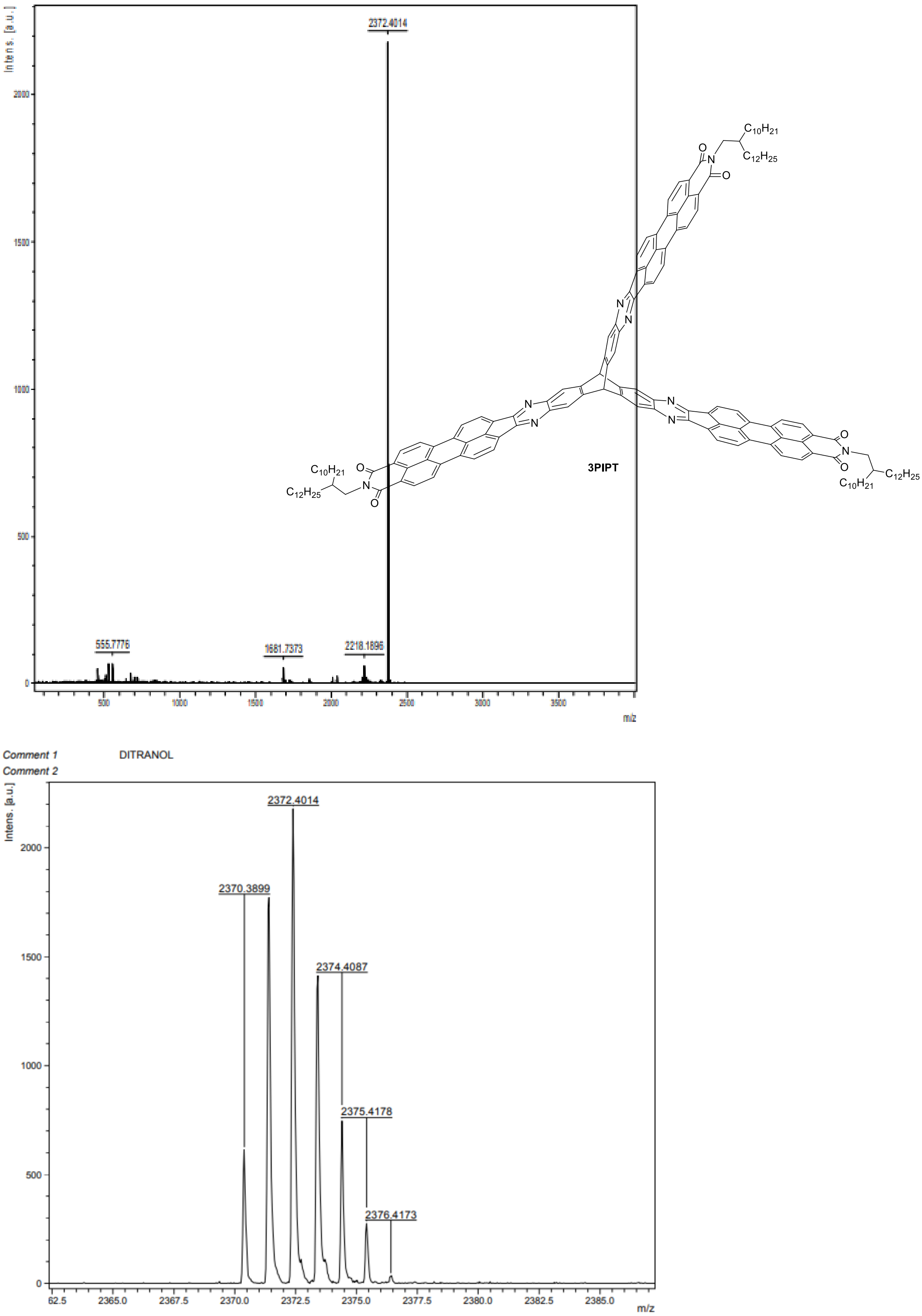


Figure S17. MALDI-HRMS (m/z) mass spectrum of **3PIPT**.

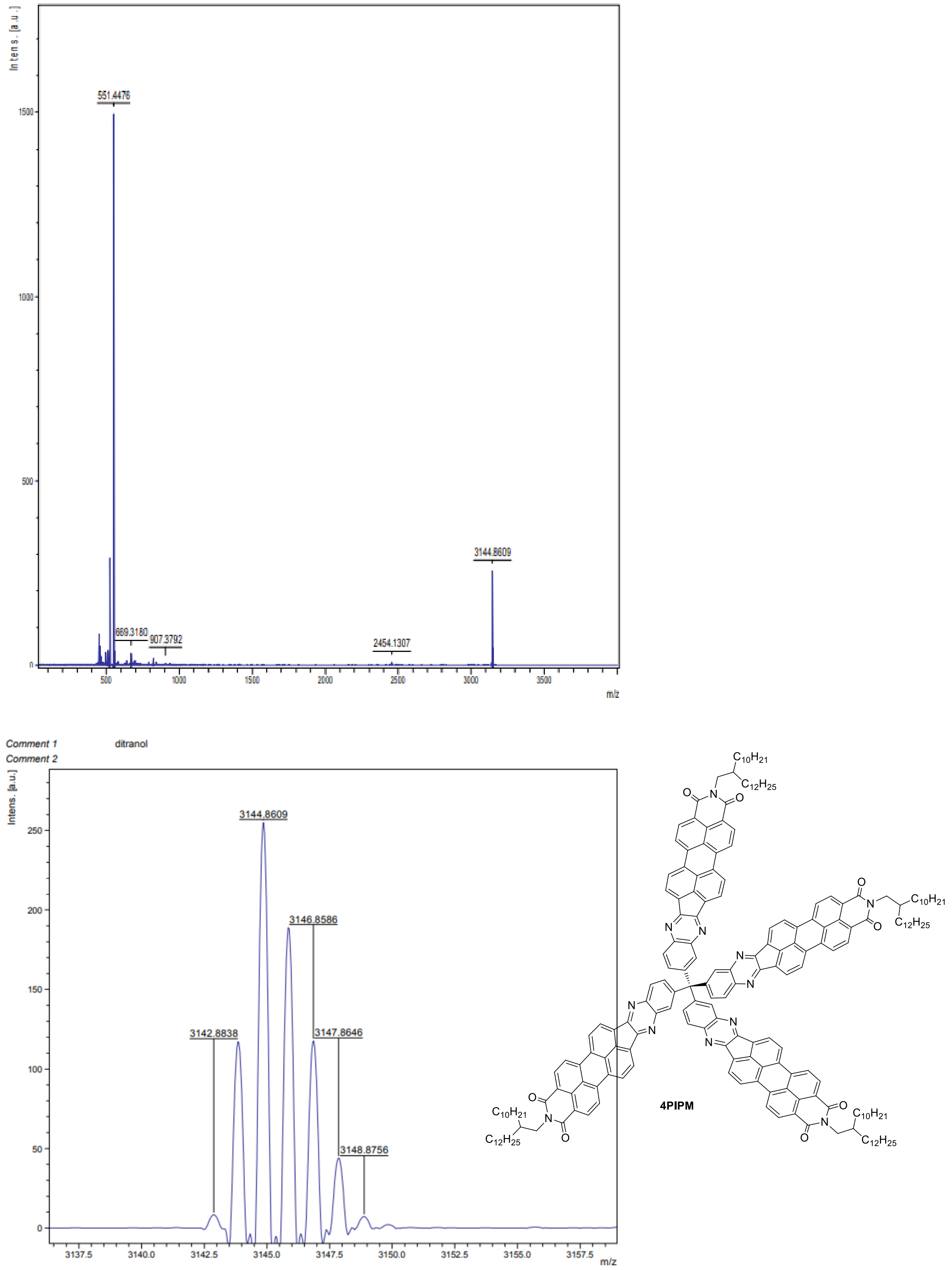


Figure S18. MALDI-HRMS (m/z) mass spectrum of **4PIPM**.

IR SPECTRA OF PIPB, 3PIPT AND 4PIPM

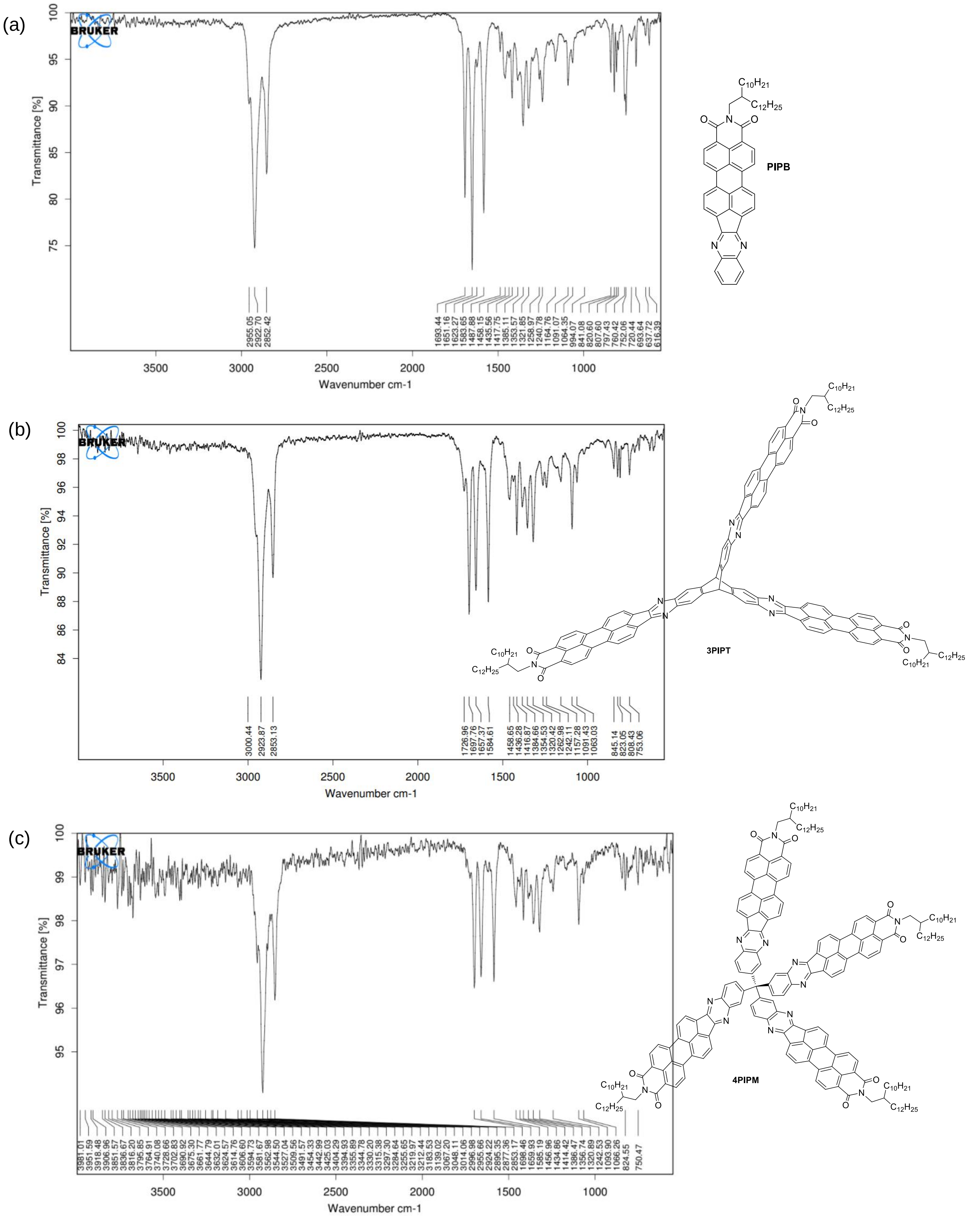


Figure S19. IR spectra of (a) **PIPB**, (b) **3PIPT** and (c) **4PIPM**.

THERMOGRAVIMETRIC ANALYSIS (TGA)

(heating at 10 °C /min under N_2)

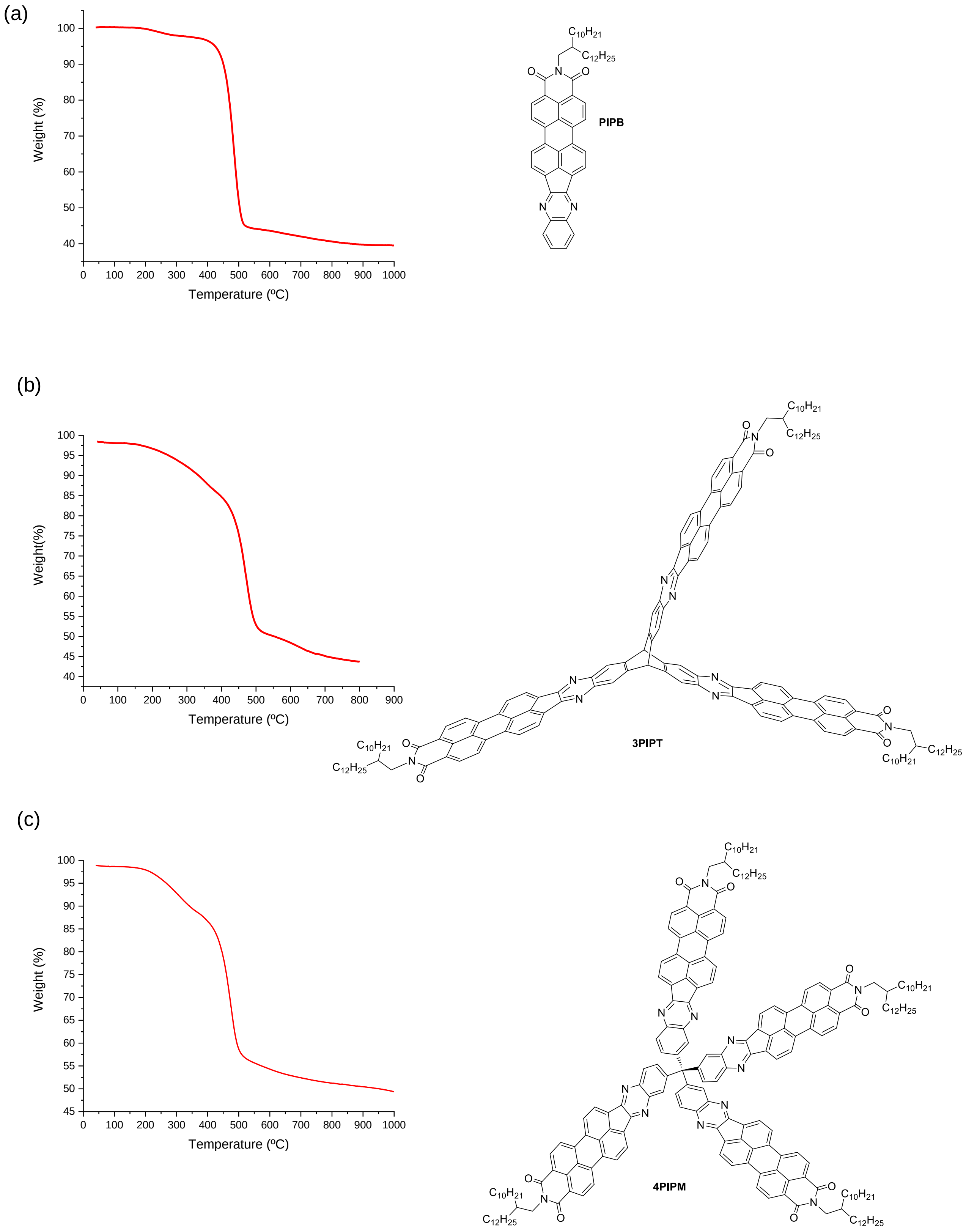
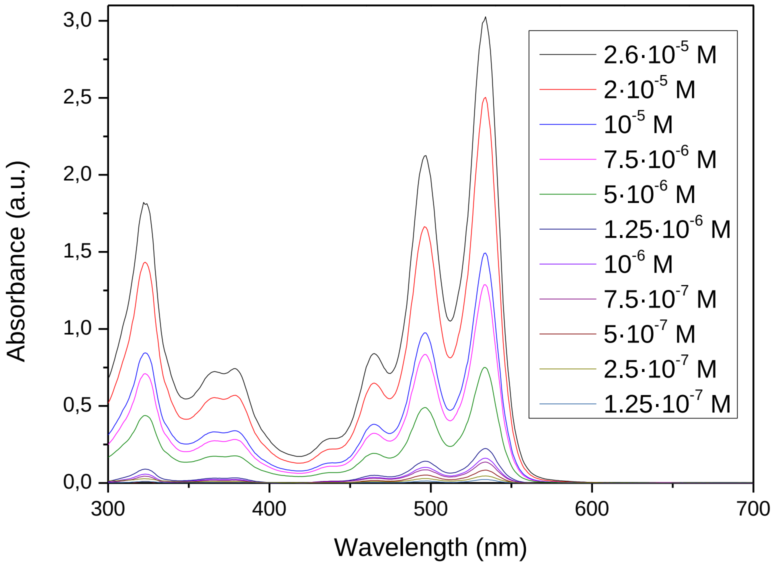
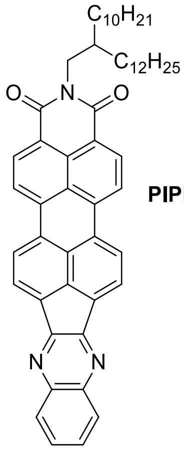


Figure S20. TGA analysis for (a) **PIPB**, (b) **3PIPT** and (c) **4PIPM**.

UV-VIS SPECTRA OF PIPB, 3PIPT AND 4PIPM





PIPB

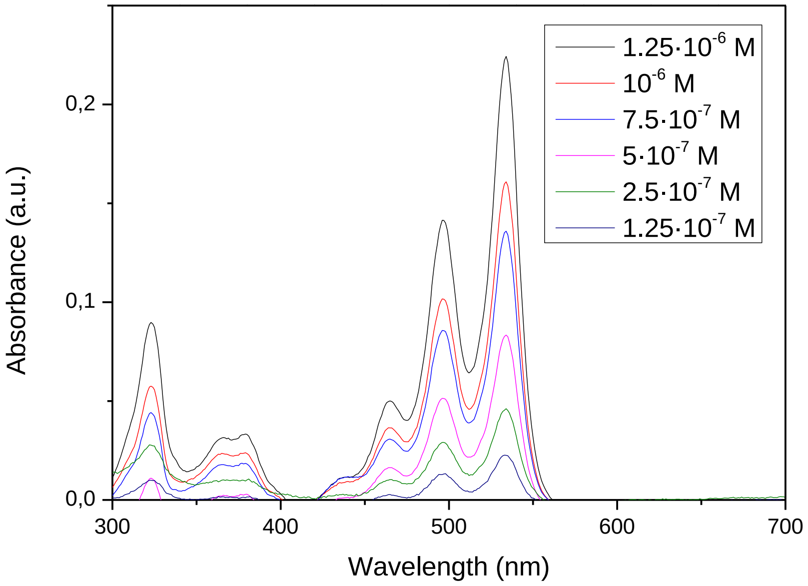


Figure S21. Solution UV-Vis spectra of **PIPB** at different concentrations.

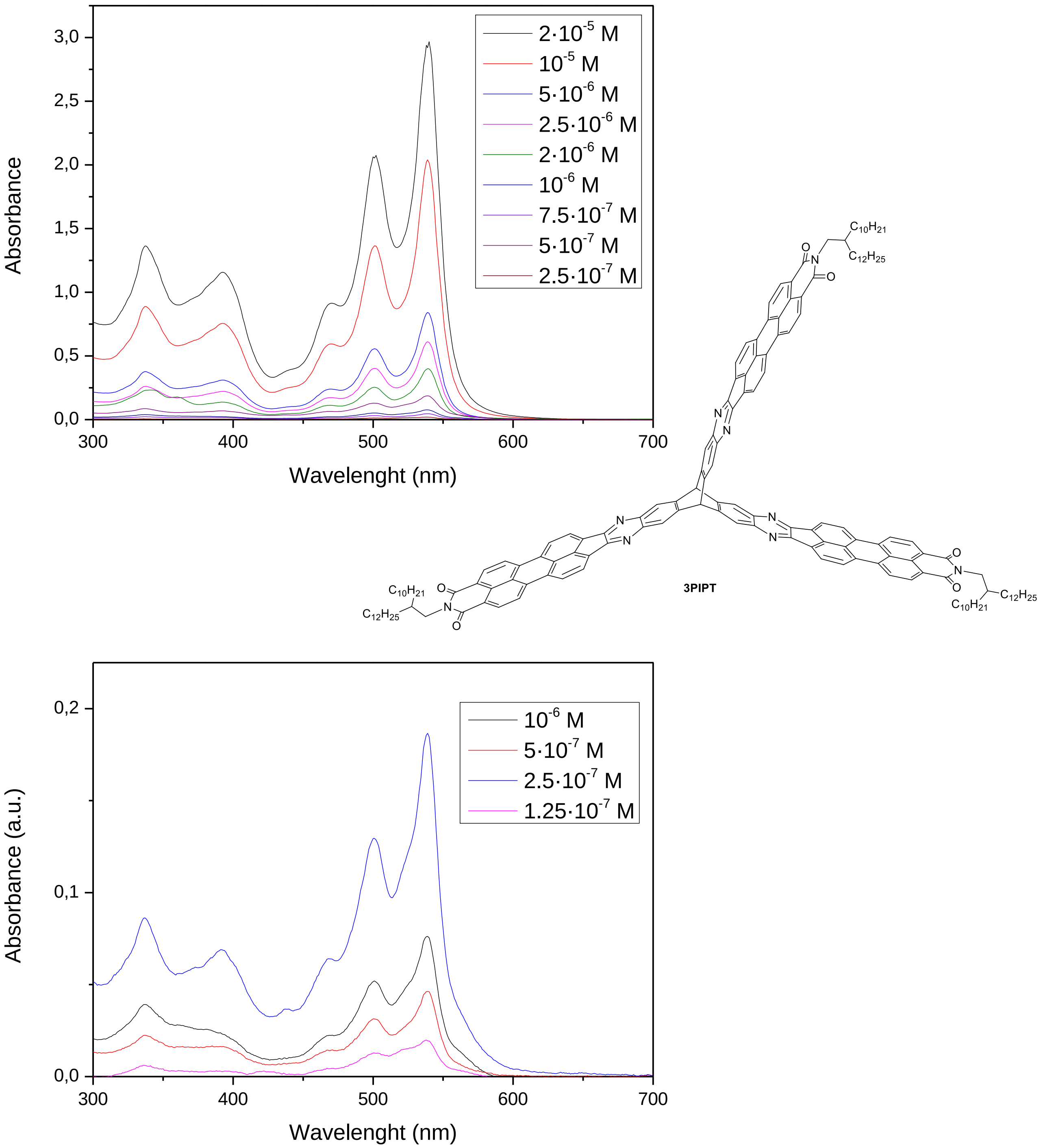


Figure S22. Solution UV-Vis spectra of **3PIPT** at different concentrations.

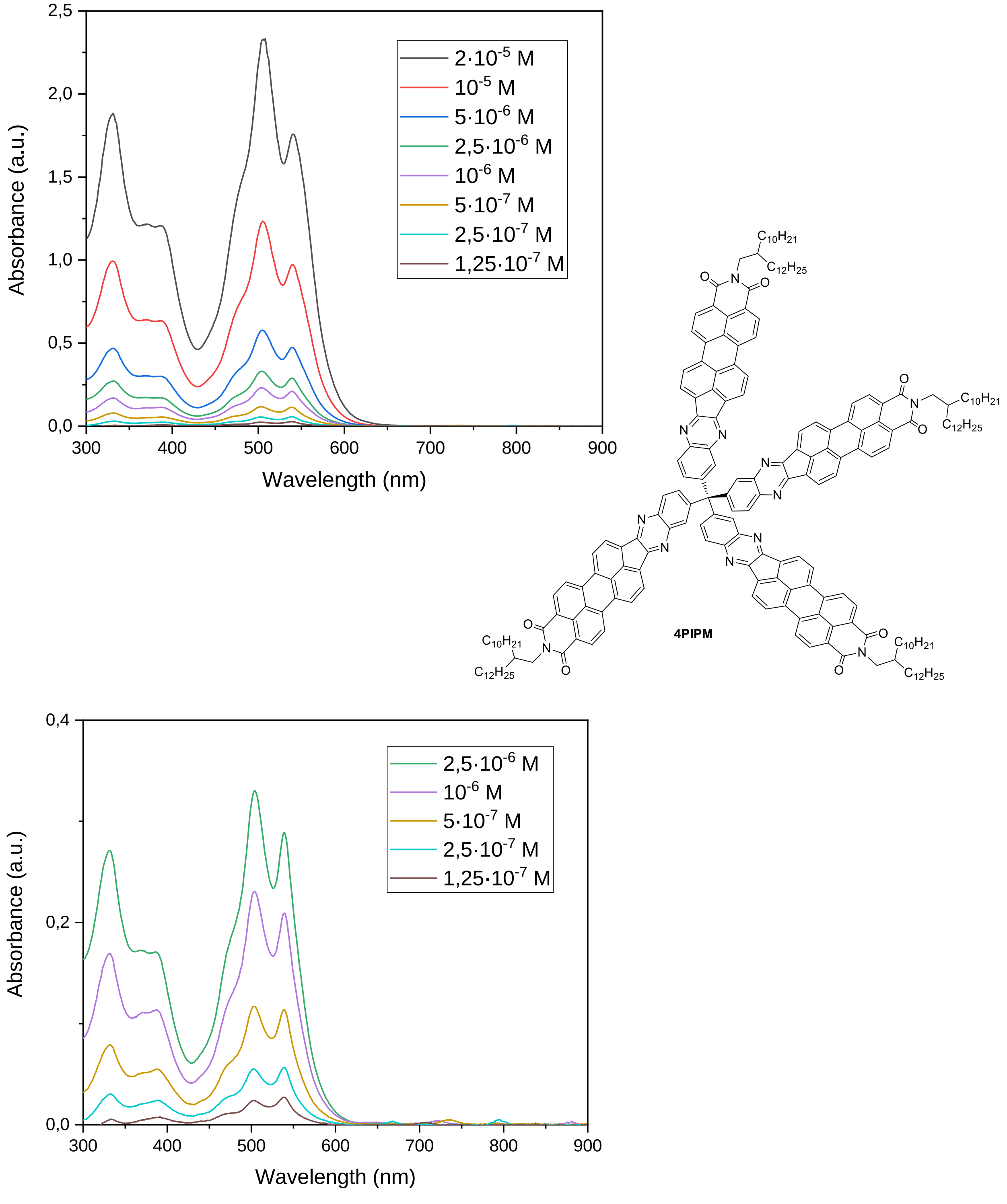


Figure S23. Solution UV-Vis spectra of **4PIPM** at different concentrations.

EMISSION SPECTRA OF PIPB, 3PIPT AND 4PIPM IN SOLUTION

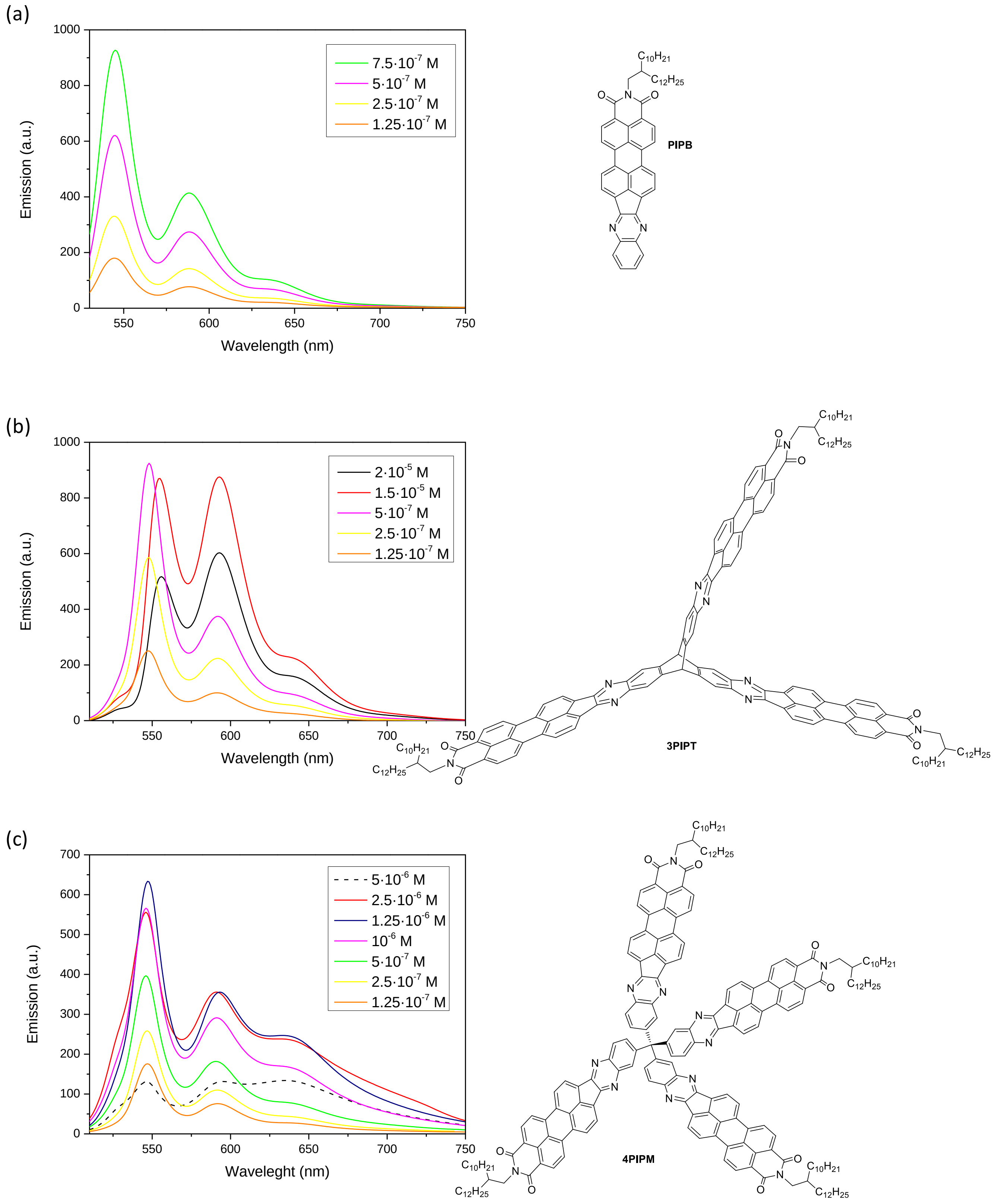


Figure S24. Solution emission spectra of (a) **PIPB**, (b) **3PIPT** and (c) **4PIPM** at different concentrations.

CYCLIC VOLTAMMETRY OF PIPB, 3PIPT AND 4PIPM

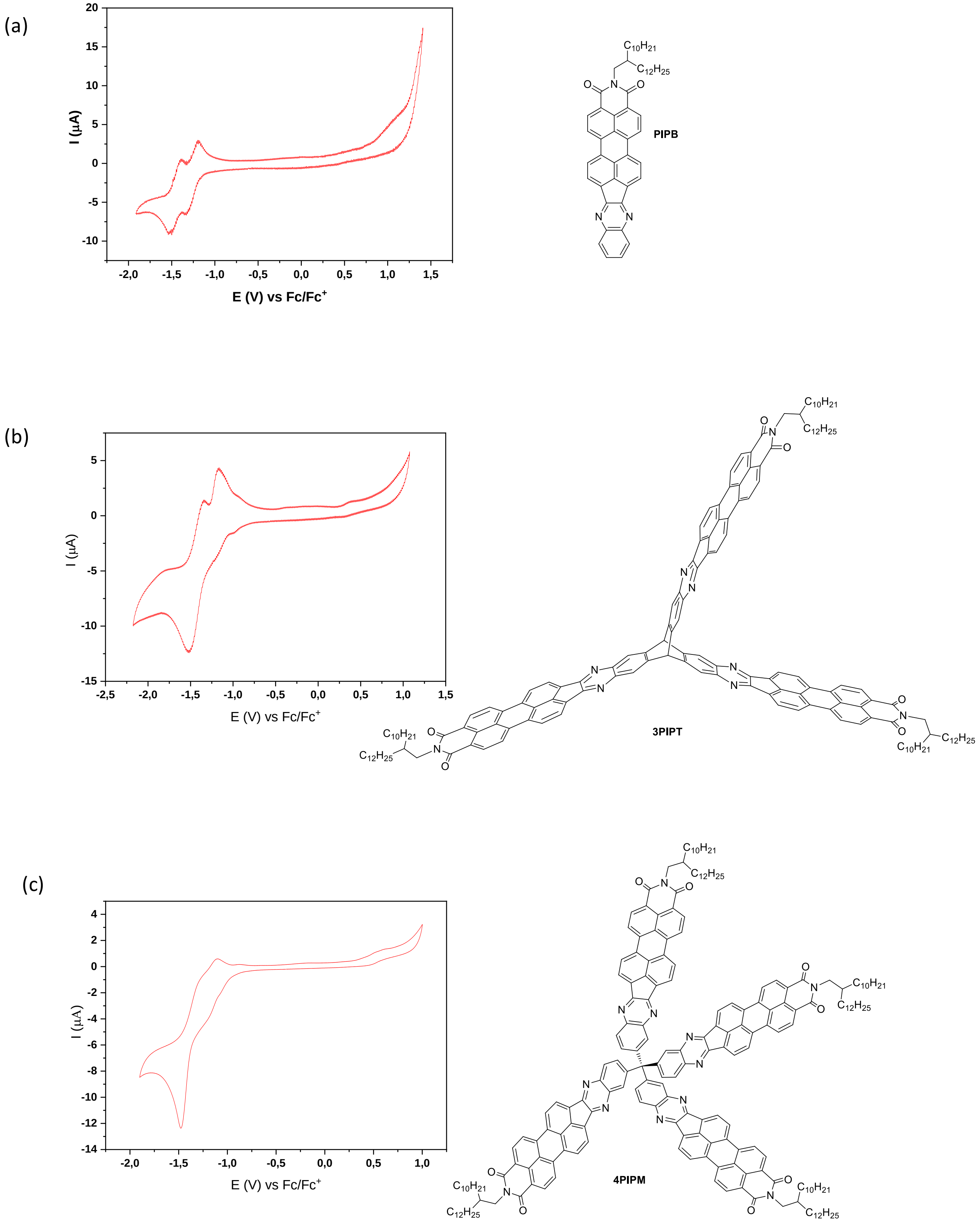


Figure S25. Cyclic voltammetry of (a) **PIPB** and 0.1 M $TBAPF_6$, (b) **3PIPT** and 0.1 M $TBAPF_6$ and (c) **4PIPM** and and 0.1 M $TBAPF_6$, all of them in dichloromethane solution.

UV-VIS ABSORPTION SPECTRA OF POLYMERS IN SOLUTION

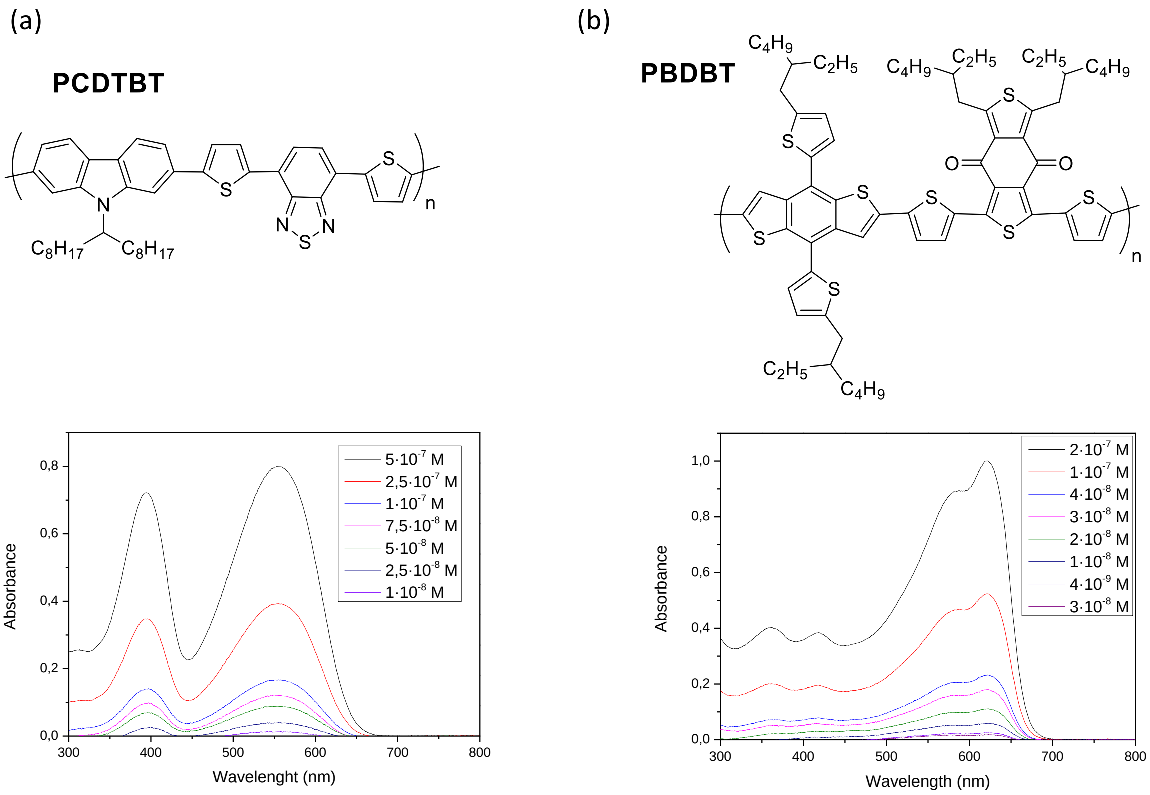


Figure S26. UV-Vis absorption spectra recorded in chloroform solutions for (a) **PCDTBT** and (b) **PBDBT**

PHOTOVOLTAIC PARAMETERS

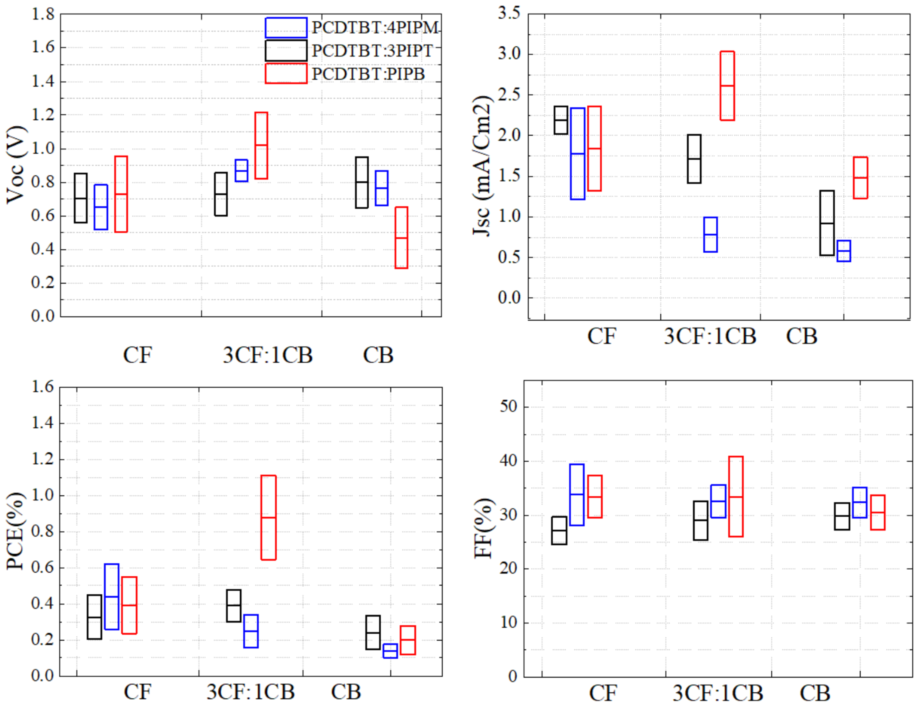


Figure S27. Box plot of the photovoltaic parameters of devices with different solvents for the different active layers **PCDTBT:PIPB** (red), **PCDTBT:3PIPT** (black) and **PCDTBT:4PIPM** (blue).

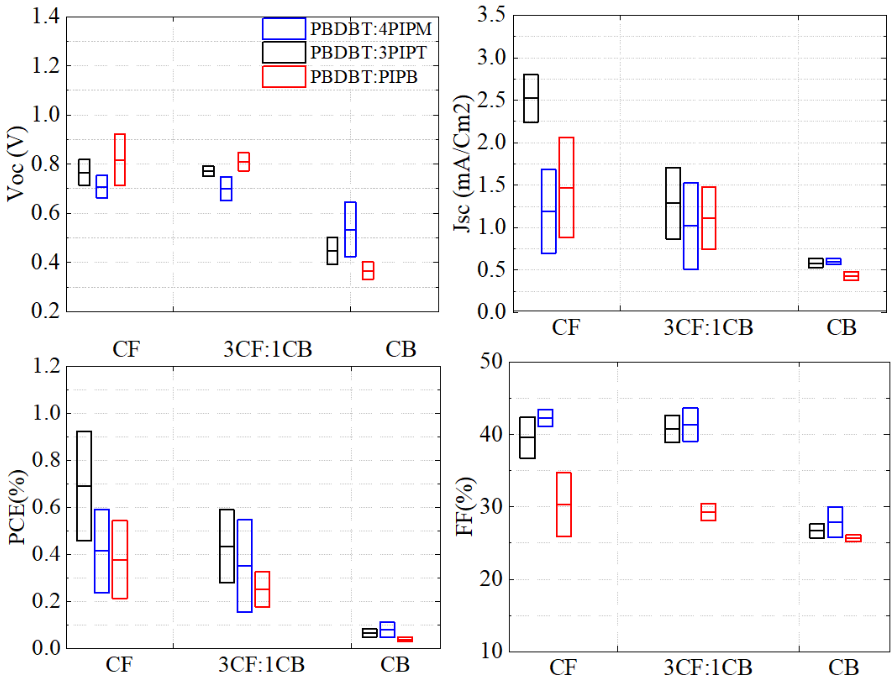


Figure S28. The box plot of the photovoltaic parameters of devices with different solvents for different active layers **PBDBT:PIPB** (red), **PBDBT:3PIPT** (black) and **PCDTBT:4PIPM** (blue).

EFFICIENCY SURFACE ON THE HANSEN SPACE

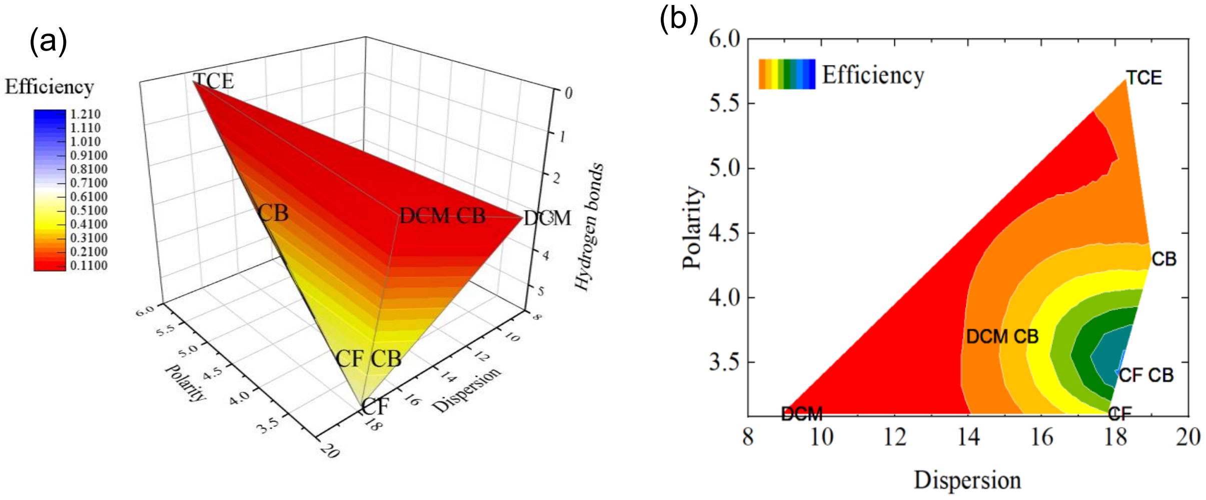


Figure S29. (a) Efficiency surface of photovoltaic devices on the Hansen solubility parameter space for different solvents used for the active layer formation. TCE: tetrachloroethane, DCM: dichloromethane, CB: chlorobenze and CF: chloroform. (b) 2D projection of the efficiency surface on the polarity/dispersion axes.

RAMAN PEAKS POSITION

Table S1. Raman peaks position of the small molecules **PIPB**, **3PIPT**, **4PIPM** and their corresponding blends with **PCDTBT** and **PBDBT**.

PCDTBT	4PIPM	3PIPT	PIPB	PCDTBT:PIPB	PCDTBT:3PIPT	PCDTBT:4PIPM	PBDBT	PBDBT:4PIPM	PBDBT:3PIPT	PBDBT:PIPB
							379			356
544	553	561	540	546	547	546	527		561	538
							580			591
	618	625	591				692	618	623	618
	717	717	708					717	713	711
842				844	844	842				
871				874	875	874	785			
1077	1066	1065	1068	1068	1066	1063	1073	1065	1075	1065
	1096	1095	1093					1091	1091	1093
1270				1272		1208	1195			
-----	1291	1291	1291	1291	1291	1289	1296	1289	1291	1289
1348	-----		-----	1350	1352	1350				
1372	1376	1379	1375	1376	1377	1374		1374	1377	1374
1447	1460	1460	1459	1449	1449	1449	1430	1428	1429	1427
								1459	1459	1457
1541	------	-----	-----	1543	1543	1541			1489	1488
-----	1588	1587	1585	1587	1587	1587		1585	1540	
							1645		1585	1584
1622	1628	1628	1627	1625	1627	1625	1789	1627	1628	1627

PHOTOVOLTAIC PARAMETERS OF DEVICES WITH THICKNESS GRADIENT

PBDBT:PIPB	V_{oc} (V)	J_{sc} (mA/cm^2)	FF %	PCE %	PBDBT:4PIPM	Voc (V)	Jsc (mA/cm^2)	FF %	PCE %	PBDBT:3PIPM	Voc (V)	Jsc (mA/cm^2)	FF %	PCE %
L.01	0.88	-1.79	23.93	0.38	L.01	0.75	-2.22	41.61	0.69	L.01	0.82	-2.5	41.79	0.85
R.01	0.87	-2.16	25.76	0.48	R.01	0.75	-2.06	38.56	0.59	R.01	0.76	-2.39	36.06	0.66
L.02	0.75	-1.23	27.67	0.25	L.02	0.75	-2.29	41.67	0.72	L.02	0.8	-2.15	39	0.67
R.02	0.8	-1.76	28.57	0.4	R.02	0.75	-2.36	41.64	0.74	R.02	0.78	-2.1	40.42	0.66
L.03	0.83	-0.81	27.8	0.19	L.03	0.53	-2.08	49.57	0.55	L.03	0.78	-1.74	37.8	0.51
R.03	0.76	-1.17	27.97	0.25	R.03	0.39	-2.12	29.15	0.24	R.03	0.78	-1.69	40.82	0.54
L.04	0.82	-0.8	30.44	0.2	L.04	0.08	-1.81	23.26	0.03	L.04	0.76	-1.3	38.26	0.38
R.04	1.31	0	36.47	0	R.04	0.44	-1.85	34.21	0.28	R.04	0.75	-1.29	39.94	0.38
L.05	0.82	-0.85	29.56	0.2	L.05	0.71	-0.92	40.93	0.27	L.05	0.75	-0.97	40.46	0.29
R.05	0.8	-0.87	29.16	0.2	R.05	0.71	-1.12	39.2	0.31	R.05	0.75	-0.97	40.89	0.3
L.06	0.83	-1.01	29.76	0.25	L.06	0.68	-0.6	41.5	0.17	L.06	0.75	-0.82	42.47	0.26
R.06	0.83	-1.07	29.77	0.26	R.06	0.69	-0.68	40.09	0.19	R.06	0.73	-0.82	39.33	0.24
L.07	0.87	-1.1	29.94	0.29	L.07	0.69	-0.71	41.5	0.2	L.07	0.76	-0.98	44.27	0.33
R.07	0.8	-1.04	30.21	0.25	R.07	0.69	-0.69	42	0.2	R.07	0.75	-0.97	41.18	0.3
L.08	0.86	-1.1	29.69	0.28	L.08	0.71	-0.89	40.9	0.26	L.08	0.79	-1.31	42.99	0.44
R.08	0.79	-0.88	29.87	0.21	R.08	0.69	-0.8	42.03	0.23	R.08	0.76	-1.22	41.85	0.39
L.09	0.84	-1.07	30.24	0.27	L.09	0.72	-1.01	40.97	0.3	L.09	0.79	-1.26	41.69	0.41
R.09	0.75	-0.83	29.6	0.18	R.09	0.69	-0.85	42.31	0.25	R.09	0.78	-1.34	42.78	0.44
L.10	0.8	-0.9	30.22	0.22	L.10	0.71	-0.99	39.06	0.27	L.10	0.78	-1.22	41.56	0.39
R.10	1.24	0	0	0	R.10	0.69	-0.81	42.34	0.24	R.10	0.78	-1.24	41.93	0.4
L.11	0.78	-0.85	30.37	0.2	L.11	0.71	-0.97	40.44	0.28	L.11	0.78	-1.19	40.18	0.37
R.11	0.52	0	0	0	R.11	1.38	0	87.88	0	R.11	1.35	0	69.84	0
L.12	0.78	-0.9	29.52	0.21	L.12	0.69	-0.77	39.61	0.21	L.12	0.78	-1.11	40.87	0.35
R.12	1.46	0	80.97	0	R.12	1.49	0	77.02	0	R.12	1.42	0	70.85	0

Table S2. Photovoltaic parameters of devices based on **PBDBT** with thickness gradient. L and R stand for left and right sides of the sample.

PCDTBT:PIPB	Voc (V)	Jsc (mA/cm^2)	FF %	PCE %	PCDTBT:4PIPM	Voc (V)	Jsc (mA/cm^2)	FF %	PCE %	PCDTBT:3PIPM	Voc (V)	Jsc (mA/cm^2)	FF %	PCE %
L.01	0.79	-2.96	47.35	1.11	L.01	0.88	-1.73	31.05	0.47	L.01	0.06	-2.23	21.06	0.03
R.01	1.08	-2.98	34.51	1.11	R.01	0.24	-1.77	27.01	0.11	R.01	0.41	-2.07	32.71	0.28
L.02	1.16	-3.02	34.63	1.22	L.02	0.92	-1.44	32.82	0.44	L.02	0.49	0	46.26	0
R.02	1.15	-3.01	29.16	1.01	R.02	0.84	-1.48	30.26	0.38	R.02	0.4	-2.15	28.55	0.25
L.03	0.22	-2.98	26.71	0.18	L.03	0.91	-1.14	32.22	0.33	L.03	0.53	-2.32	44.32	0.55
R.03	1.11	-3.01	34.58	1.16	R.03	0.43	-1.2	28.56	0.15	R.03	1.2	-2.01	9.03	0.22
L.04	1.14	-2.83	29.85	0.96	L.04	0.73	-0.85	35.98	0.23	L.04	0.67	-2.31	32.14	0.49
R.04	1.12	-2.91	22.22	0.73	R.04	0.91	-0.89	32	0.26	R.04	0.27	-2.22	25.93	0.15
L.05	0.57	-2.7	30.07	0.47	L.05	0.9	-0.69	32.99	0.2	L.05	0.82	-2.27	30.34	0.56
R.05	0.65	-2.71	49.43	0.88	R.05	0.9	-0.71	32.73	0.21	R.05	0.53	-2.19	34.75	0.41
L.06	1.15	-2.5	31.48	0.91	L.06	0.88	-0.62	34.2	0.19	L.06	0.61	-2.2	30.33	0.41
R.06	1.07	-2.46	30.94	0.81	R.06	0.48	-0.63	26.56	0.08	R.06	0.43	-2.17	31.39	0.29
L.07	0.18	-2.24	0	0.75	L.07	0.86	-0.7	32.94	0.2	L.07	0.13	-2.18	0	0.43
R.07	0.16	-2.06	0	0.67	R.07	0.67	-0.68	28.53	0.13	R.07	0.84	-2.12	19.65	0.35
L.08	1.14	-2.08	30.8	0.73	L.08	0.88	-0.77	35.4	0.24	L.08	0.91	-1.9	20.75	0.36
R.08	0.33	-1.99	25.25	0.17	R.08	0.91	-0.74	34.82	0.23	R.08	0.67	-1.98	30.96	0.41
L.09	1.45	-1.9	18.23	0.5	L.09	0.9	-0.75	34.47	0.23	L.09	0.68	-1.69	31.14	0.36
R.09	1.06	-1.9	28.98	0.58	R.09	0.9	-0.73	34.98	0.23	R.09	0.67	-1.83	29.1	0.36
L.10	0.25	0	0	0	L.10	0.88	-0.72	23.25	0.15	L.10	0.87	-1.26	29.47	0.32
R.10	0.04	0	0	0	R.10	0.9	-0.68	34.9	0.21	R.10	0.79	-1.61	26	0.33
L.11	1.08	-1.87	29.64	0.6	L.11	0.88	-0.68	34.35	0.2	L.11	0.49	-1.09	28.89	0.16
R.11	0.22	0	0	0	R.11	0.5	0	0	0	R.11	1.42	0	0	0
L.12	1.12	-1.61	0.33	0.01	L.12	0.84	-0.76	31.15	0.2	L.12	0.53	-1.52	31.99	0.26
R.12	0.29	0	0	0	R.12	0.49	0	0	0	R.12	0.45	0	82.21	0

Table S3. Photovoltaic parameters of devices based on **PCDTBT** with thickness gradient.

ANOVA STUDY

Table S4. ANOVA studies of Hansen solubility parameters, different D:A ratios for **PCDTBT:PIPB**, different solvents for different active layers and different donors for different acceptors.

F factor	Parameter
45.1	Different **solvents** for **PCDTBT:PIPB** devices
44.1	Different **solvents** for **PBDBT:PIPB** devices
54.5	Different **solvents** for **PBDBT:3PIPT**
8.2	Different **solvents** for **PCDTBT:3PIPT**
11.9	Different **solvents** for **PBDBT:4PIPM**
24.6	Different **solvents** for **PCDTBT:4PIPM**
0.78	Different **donors** for **3PIPT**
4.2	Different **donors** for **4PIPM**
120.3	Different **donors** for **PIPB**
114.8	Hydrogen bonds
71.4	Polarity
114.8	Dispersion

Table S5. Quantitive PL quenching of the blends **PCDTBT:PIPB**, **PCDTBT:3PIPT** and **PCDTBT:4PIPM** to their acceptors and donors.

	PCDTBT:PIPB	**PCDTBT:3PIPT**	**PCDTBT:4PIPM**	**PBDBT:PIPB**	**PBDBT:3PIPT**	**PBDBT:4PIPM**
Acceptors	0.03	0.85	**3.28**	0.02	0.14	0.28
Donors	0.04	0.21	0.44	**64.2**	**117.5**	**129.5**

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