Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

The effect of diketopyrrolopyrrole (DPP) group inclusion in *p*-cyanophenyl end-capped oligothiophene used as dopant in P3HT:PCBM BHJ solar cells

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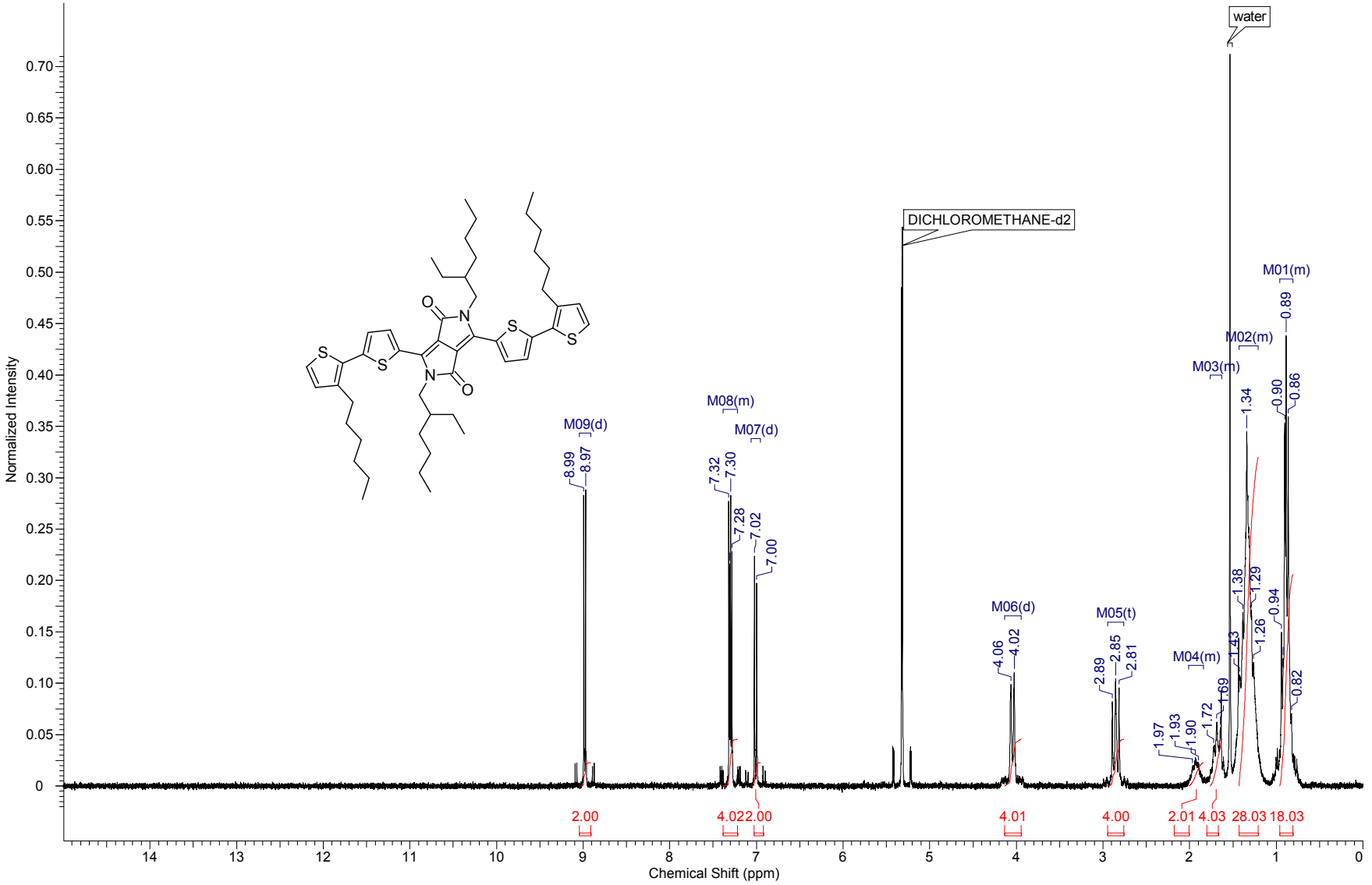
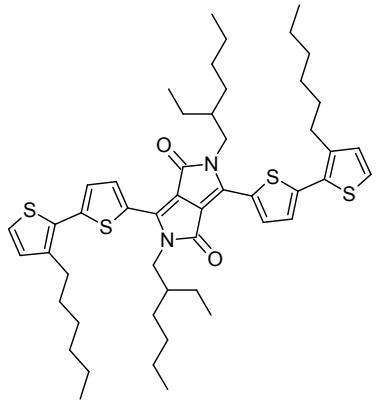
SUPPLEMENTARY INFORMATION

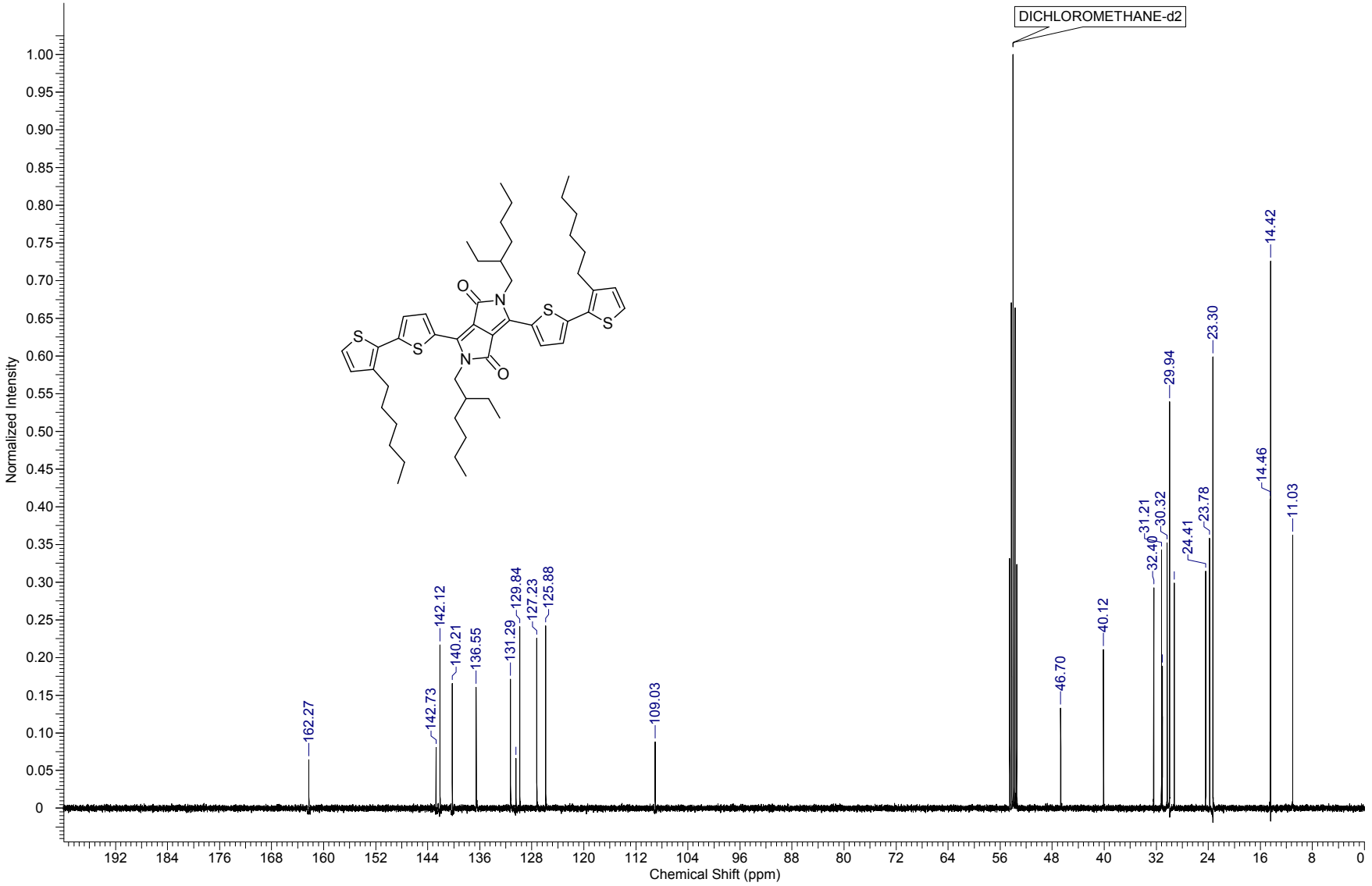
^{1}H NMR spectrum of compound 2



No.	Shift1 (ppm)	H's	Type	J (Hz)	Multiplet1	(ppm)
1	0.89	18	m	-	M01	[0.81 .. 0.96]
2	1.34	28	m	-	M02	[1.21 .. 1.43]
3	1.67	4	m	-	M03	[1.63 .. 1.76]
4	1.93	2	m	-	M04	[1.84 .. 2.01]
5	2.85	4	t	7.50	M05	[2.76 .. 2.94]
6	4.04	4	d	7.55	M06	[3.94 .. 4.14]
7	7.01	2	d	5.29	M07	[6.95 .. 7.06]
8	7.30	4	m	-	M08	[7.22 .. 7.38]
9	8.98	2	d	4.15	M09	[8.91 .. 9.05]



^{13}C NMR spectrum of compound 2



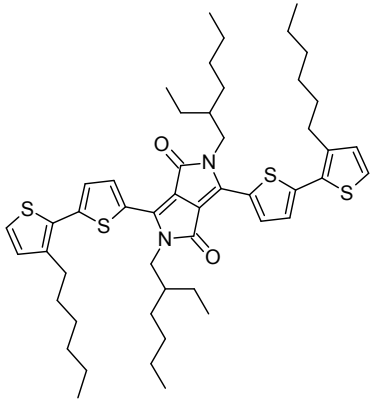
No.	(ppm)	(Hz)	Height
1	11.03	1109.3	0.3623
2	14.42	1451.1	0.7258
3	14.46	1454.8	0.4102
4	23.30	2343.9	0.5988
5	23.78	2393.1	0.3585

No.	(ppm)	(Hz)	Height
6	24.41	2456.2	0.3147
7	29.23	2941.1	0.2987
8	29.94	3012.2	0.5392
9	30.32	3050.4	0.3519
10	31.06	3125.2	0.1884

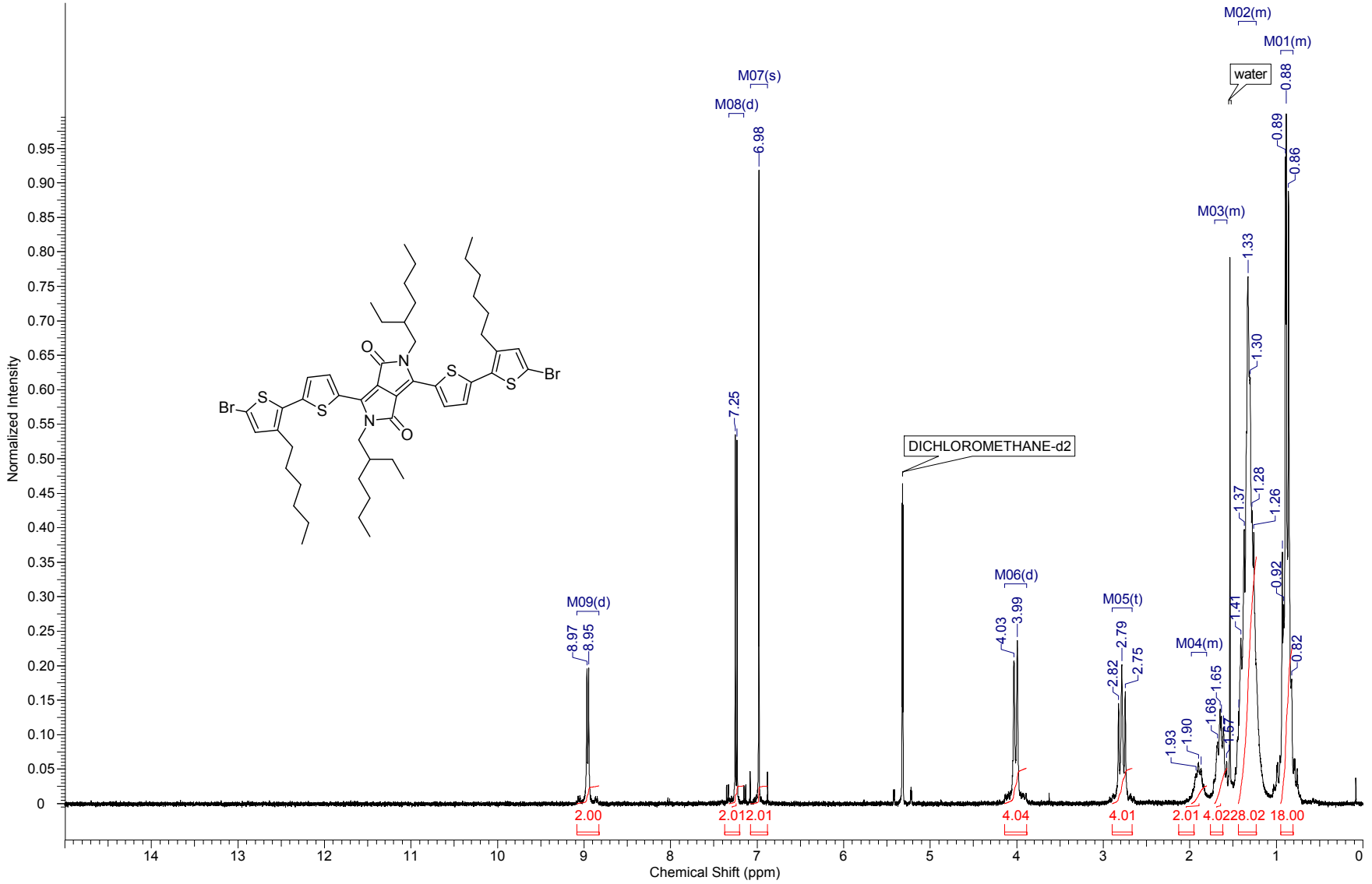
No.	(ppm)	(Hz)	Height
11	31.21	3139.9	0.3423
12	32.40	3259.4	0.2926
13	40.12	4037.1	0.2105
14	46.70	4698.8	0.1331
15	109.03	10969.5	0.0879

No.	(ppm)	(Hz)	Height
16	125.88	12664.9	0.2421
17	127.23	12801.3	0.2256
18	129.84	13064.0	0.2408
19	130.43	13122.6	0.0662
20	131.29	13209.9	0.1710

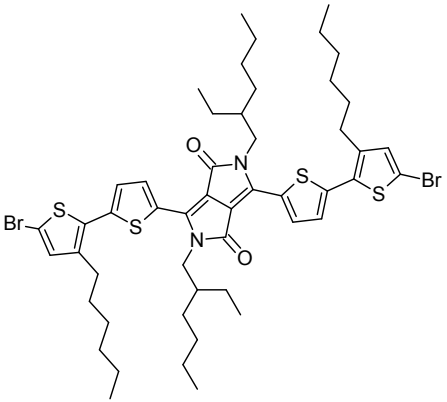
No.	(ppm)	(Hz)	Height
21	136.55	13738.9	0.1604
22	140.21	14107.1	0.1657
23	142.12	14298.6	0.2166
24	142.73	14360.2	0.0807
25	162.27	16326.3	0.0644



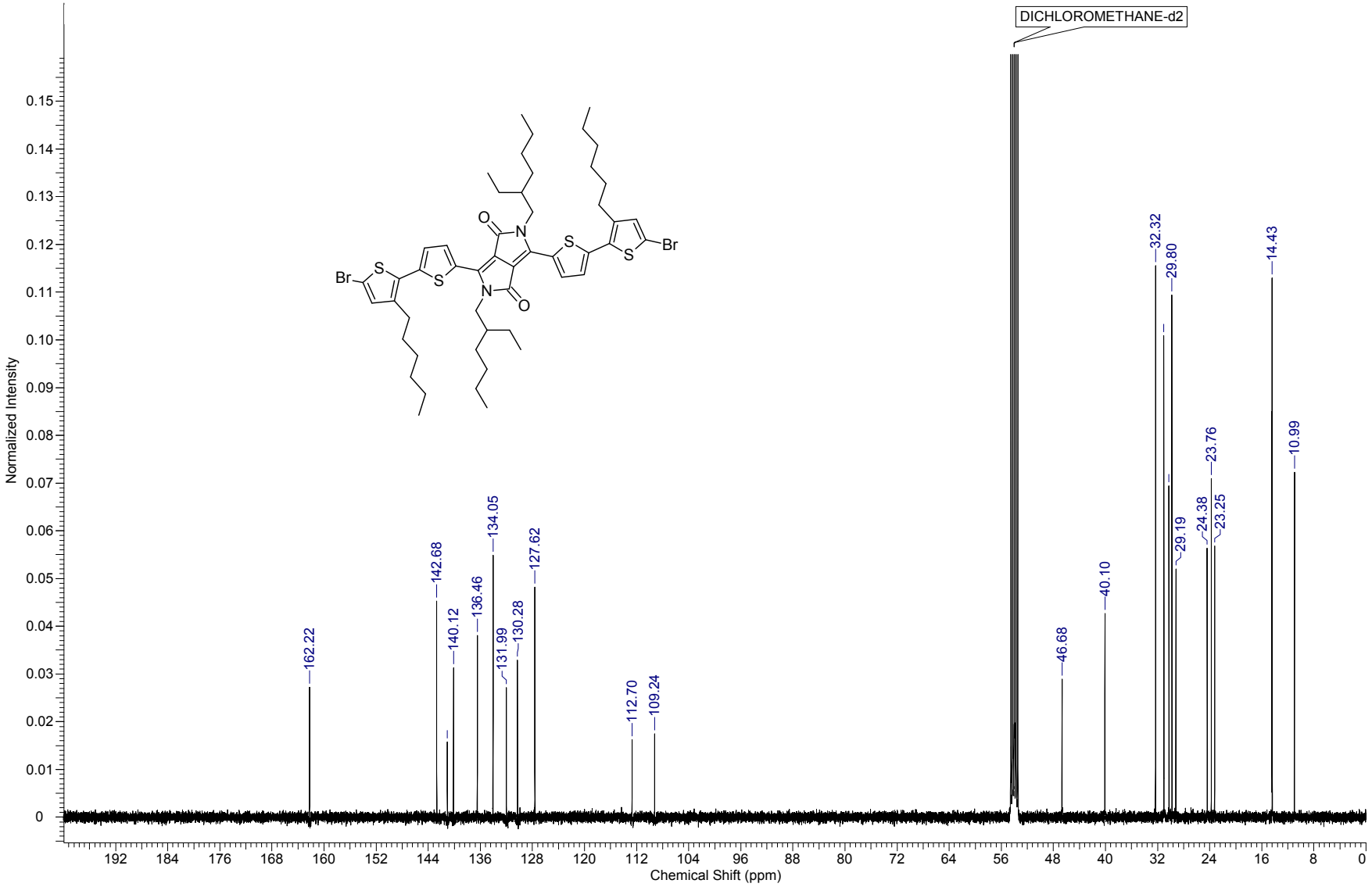
^{1}H NMR spectrum of compound 3



No.	Shift1 (ppm)	H's	Type	J (Hz)	Multiplet1	Connections	(ppm)
1	0.88	18	m	-	M01	-	[0.81 .. 0.95]
2	1.34	28	m	-	M02	-	[1.23 .. 1.44]
3	1.63	4	m	-	M03	-	[1.57 .. 1.71]
4	1.90	2	m	-	M04	-	[1.81 .. 1.98]
5	2.79	4	t	7.75	M05	-	[2.67 .. 2.90]
6	4.01	4	d	8.31	M06	-	[3.89 .. 4.14]
7	6.98	2	s	-	M07	-	[6.88 .. 7.08]
8	7.24	2	d	4.15	M08	M09	[7.16 .. 7.33]
9	8.96	2	d	4.15	M09	M08	[8.83 .. 9.08]



^{13}C NMR spectrum of compound 3



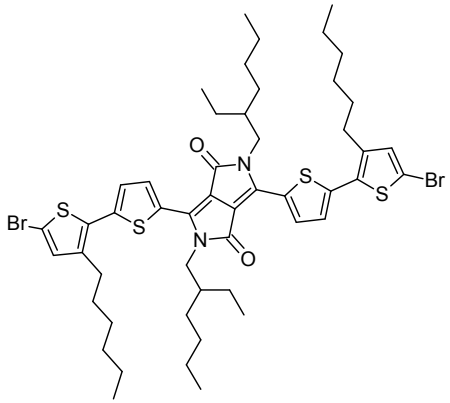
No.	(ppm)	(Hz)	Height
1	10.99	1105.6	0.0722
2	14.40	1448.9	0.0850
3	14.43	1451.9	0.1130
4	23.25	2339.5	0.0568
5	23.76	2390.1	0.0709

No.	(ppm)	(Hz)	Height
6	24.38	2453.2	0.0564
7	29.19	2936.7	0.0520
8	29.80	2998.3	0.1094
9	30.25	3043.0	0.0695
10	31.02	3120.8	0.0423

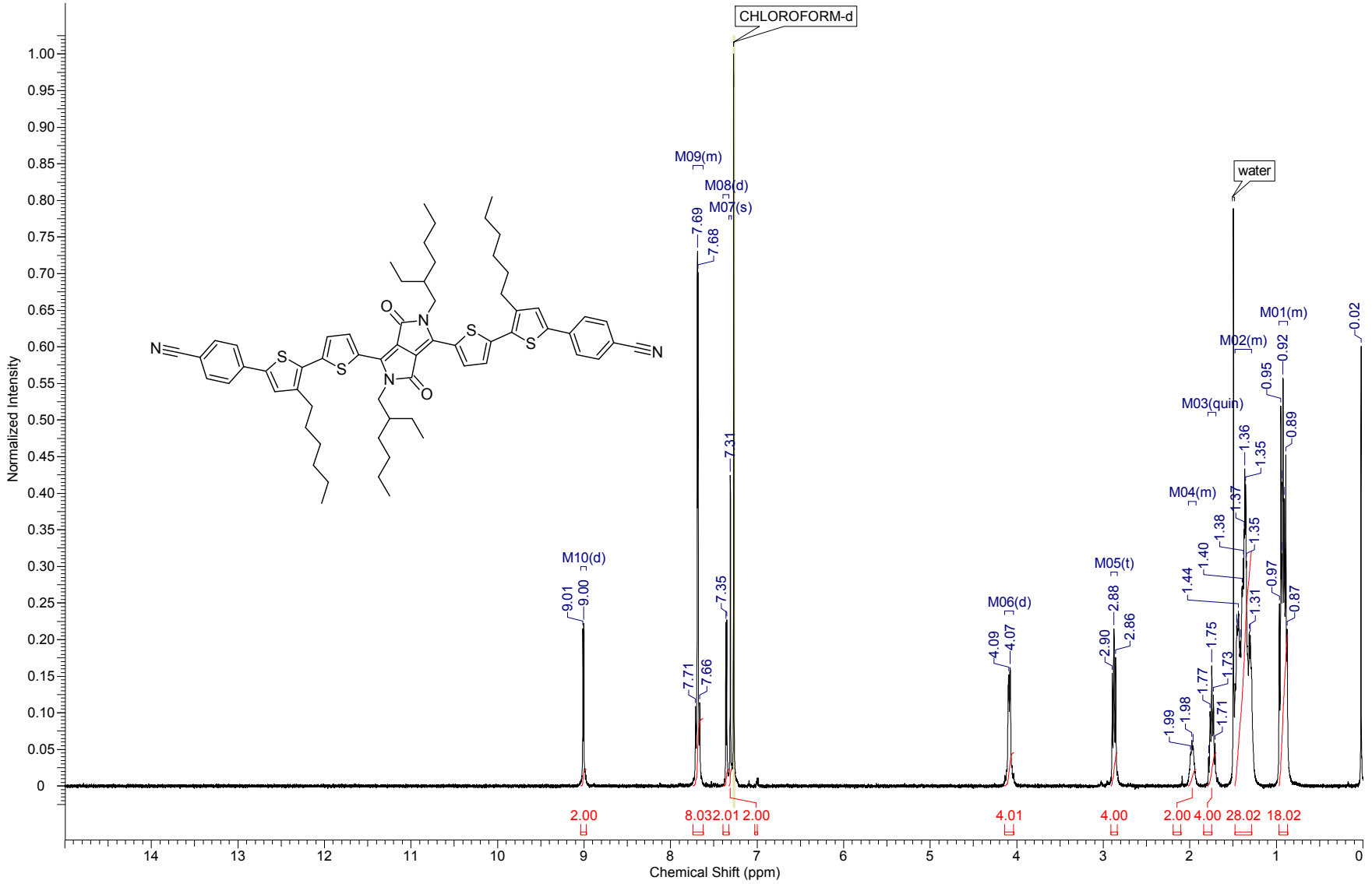
No.	(ppm)	(Hz)	Height
11	31.03	3122.3	0.1009
12	32.32	3252.1	0.1156
13	40.10	4034.1	0.0427
14	46.68	4696.6	0.0289
15	109.24	10990.8	0.0175

No.	(ppm)	(Hz)	Height
16	112.70	11339.3	0.0162
17	127.62	12840.2	0.0482
18	130.28	13108.0	0.0329
19	131.99	13280.4	0.0271
20	134.05	13487.2	0.0548

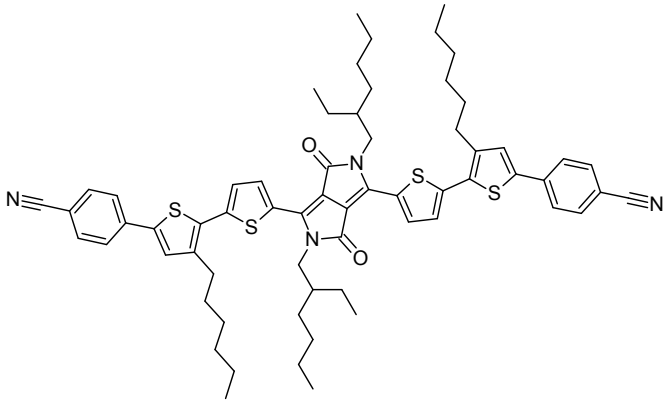
No.	(ppm)	(Hz)	Height
21	136.46	13729.3	0.0381
22	140.12	14098.3	0.0313
23	141.07	14193.0	0.0157
24	142.68	14355.8	0.0452
25	162.22	16321.1	0.0272



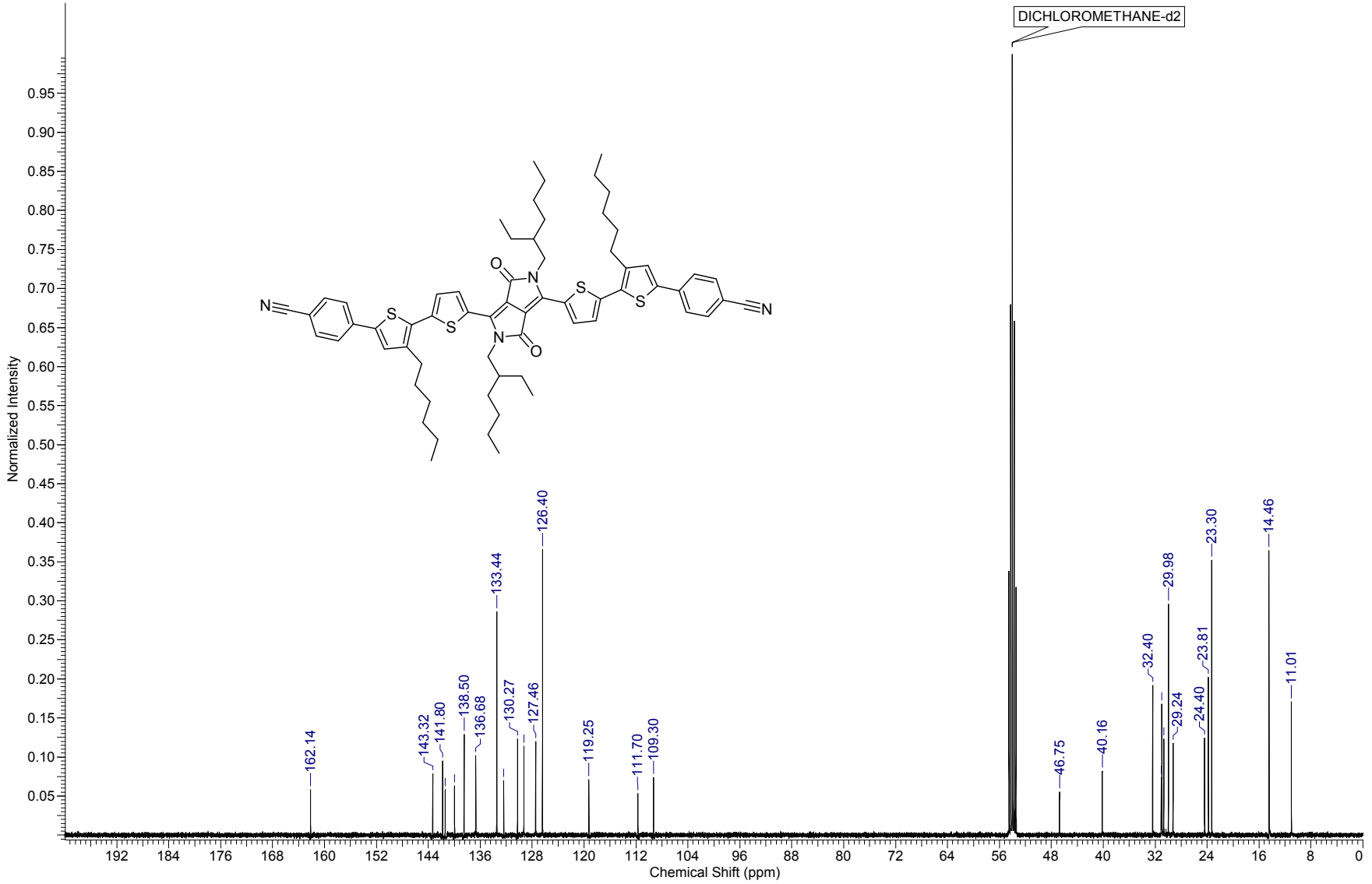
^{1}H NMR spectrum of DPP-(2TPhCN)$_2$



No.	Shift1 (ppm)	H's	Type	J (Hz)	Multiplet1	Connections	(ppm)
1	0.92	18	m	-	M01	-	[0.87 .. 0.97]
2	1.38	28	m	-	M02	-	[1.29 .. 1.48]
3	1.75	4	quin	7.59, 7.59	M03		[1.70 .. 1.79]
4	1.98	2	m	-	M04	-	[1.93 .. 2.02]
5	2.88	4	t	7.78	M05	-	[2.84 .. 2.91]
6	4.08	4	d	7.53	M06		[4.04 .. 4.14]
7	7.31	2	s	-	M07	-	[7.29 .. 7.32]
8	7.36	2	d	4.02	M08	M10	[7.33 .. 7.39]
9	7.69	8	m	-	M09	-	[7.62 .. 7.74]
10	9.01	2	d	4.02	M10	M08	[8.98 .. 9.04]



^{13}C NMR spectrum of DPP-(2TPhCN)$_2$



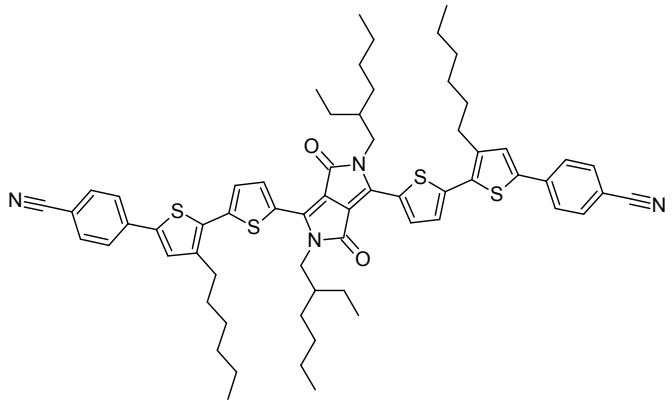
No.	(ppm)	(Hz)	Height
1	11.01	1107.8	0.1704
2	14.46	1454.8	0.3646
3	23.30	2343.9	0.3521
4	23.81	2395.3	0.2020
5	24.40	2455.4	0.1240
6	29.24	2941.8	0.1177

No.	(ppm)	(Hz)	Height
7	29.98	3015.9	0.2958
8	30.68	3087.1	0.1230
9	30.97	3116.4	0.1680
10	31.06	3125.2	0.0735
11	31.08	3127.4	0.0734
12	32.40	3259.4	0.1916

No.	(ppm)	(Hz)	Height
13	40.16	4040.7	0.0820
14	46.75	4703.9	0.0552
15	109.30	10996.7	0.0740
16	111.70	11238.0	0.0532
17	119.25	11998.0	0.0709
18	126.40	12717.7	0.3654

No.	(ppm)	(Hz)	Height
19	127.46	12824.1	0.1198
20	129.27	13006.0	0.1138
21	130.27	13106.5	0.1231
22	132.37	13317.8	0.0701
23	133.44	13425.6	0.2858
24	136.68	13751.3	0.1021

No.	(ppm)	(Hz)	Height
25	138.50	13934.7	0.1288
26	139.95	14080.7	0.0629
27	141.41	14227.4	0.0579
28	141.80	14267.0	0.0946
29	143.32	14419.6	0.0784
30	162.14	16313.8	0.0582



Computational modelling

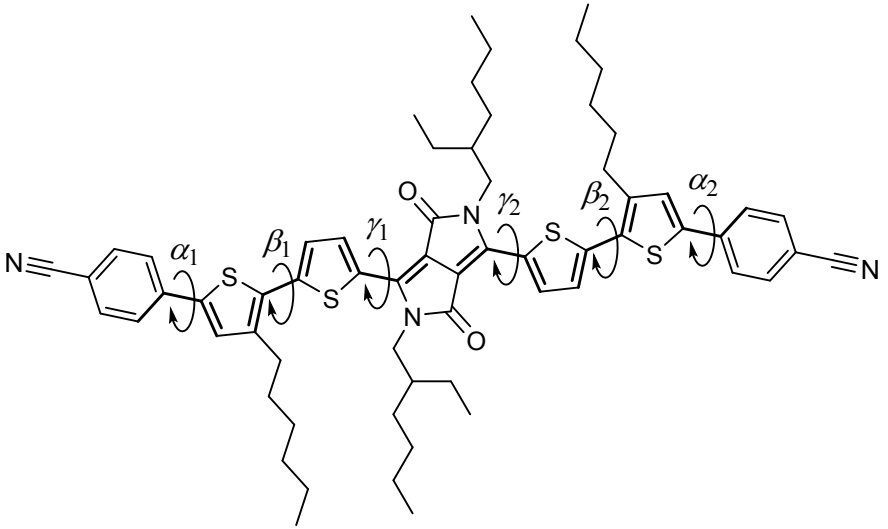


Fig. S1 Studied dihedral angles of **DPP-(2TPhCN)$_2$**.

Table S1 Dihedral angles (absolute values) of the DFT-optimized ground-state geometry of the **DPP-(2TPhCN)$_2$** calculated at the B3LYP/6-31G** level of theory.

α_1 (°)	α_2 (°)	β_1(°)	β_2(°)	γ_1 (°)	γ_2 (°)
20.3	23.3	166.7.	153.1	9.1	1.1

Table S2 Contributions (%) of the whole backbone, separate thiophenes and DPP-group, and *p*-cyanophenyl end-groups to the HOMO and LUMO of **DPP-(2TPhCN)$_2$**.

HOMO				LUMO			
Backbone (thiophenes+DPP)	**Thiophenes**	**DPP**	**End-groups**	**Backbone (thiophenes+DPP)**	**Thiophenes**	**DPP**	**End-groups**
96.2	42.6	53.6	3.8	91.35	53.41	37.94	8.65

Computed absorption spectra. Calculated UV-Vis absorption spectrum of **DPP-(2TPhCN)$_2$** is shown in Figure S2. The spectrum is characterized by one dominant absorption band at a lower energy, which is associated to the $S_0 \rightarrow S_1$ transition and is HOMO → LUMO in nature. There are also two weak absorption bands at higher energies. They are assigned to the $S_0 \rightarrow S_5$ and $S_0 \rightarrow S_8$ transitions, which are mainly HOMO-2 → LUMO and HOMO-1 → LUMO+1 in nature, respectively. The exact absorption maxima, vertical transition energies, oscillator strengths, and electronic configurations related to these bands are presented in Table S3.

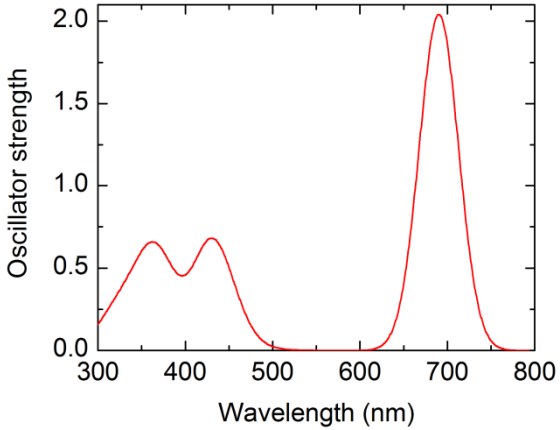


Fig. S2 UV-Vis absorption spectra of **DPP-(2TPhCN)$_2$** in chloroform calculated with TDDFT at the B3LYP/6-31G** level of theory.

Table S3 Absorption maxima (λ_{abs}), vertical transition energies (E_{vert}), oscillator strengths (f), and electronic configurations in chloroform as calculated with TDDFT at the B3LYP/6-31G** level of theory.

Compound	λ_{abs} (nm)	E_{vert} (eV)	f	Electronic configuration (%)
DPP-(2TPhCN)$_2$	690	1.80	2.04	H → L (100)
	429	2.89	0.61	H-2 → L (53); H → L+2 (45)
	366	3.40	0.58	H-6 → L (3); H-1 → L+1 (94)

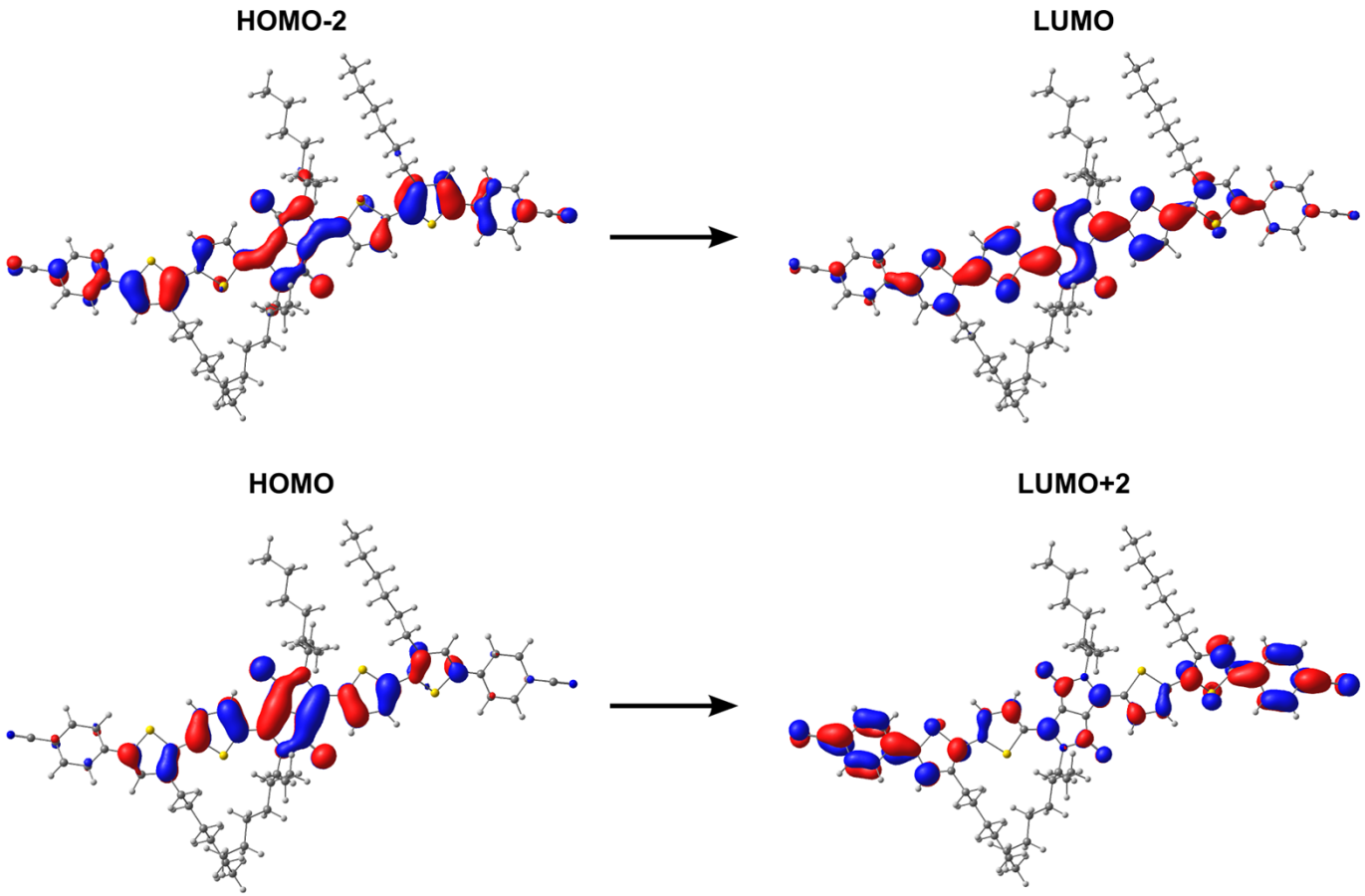


Fig. S3 Frontier molecular orbitals of **DPP-(2TPhCN)$_2$** associated to the absorption band at 429 nm (transitions: H-2 → L (53 %) and H → L+2 (45 %) calculated at the B3LYP/6-31G** level of theory (isodensity contour = 0.025).

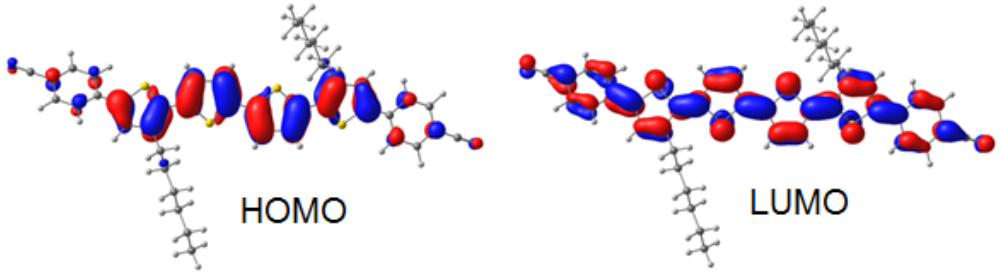


Fig. S4 Frontier molecular orbitals of **di-(*p*-CNPh)4T** calculated at the B3LYP/6-31G** level of theory (isodensity contour = 0.025).[16]

Table S4 Contributions (%) of the quaterthiophene backbone and *p*-substituted aryl end-groups to the HOMO and LUMO of **di-(*p*-CNPh)4T**.[16]

Compound	**HOMO**		**LUMO**	
	Backbone	**End-groups**	**Backbone**	**End-groups**
di-(*p*-CNPh)4T	89.9	10.1	74.87	25.13

Absorbance of the DPP-(2TPhCN)$_2$/PC$_{60}$BM solution used in the pump-probe measurements

Sample absorbance should be ~1, which is exceeded in the 0.24 mM **DPP-(2TPhCN)$_2$** solution with PC$_{60}$BM concentrations 3.52 mM and higher.

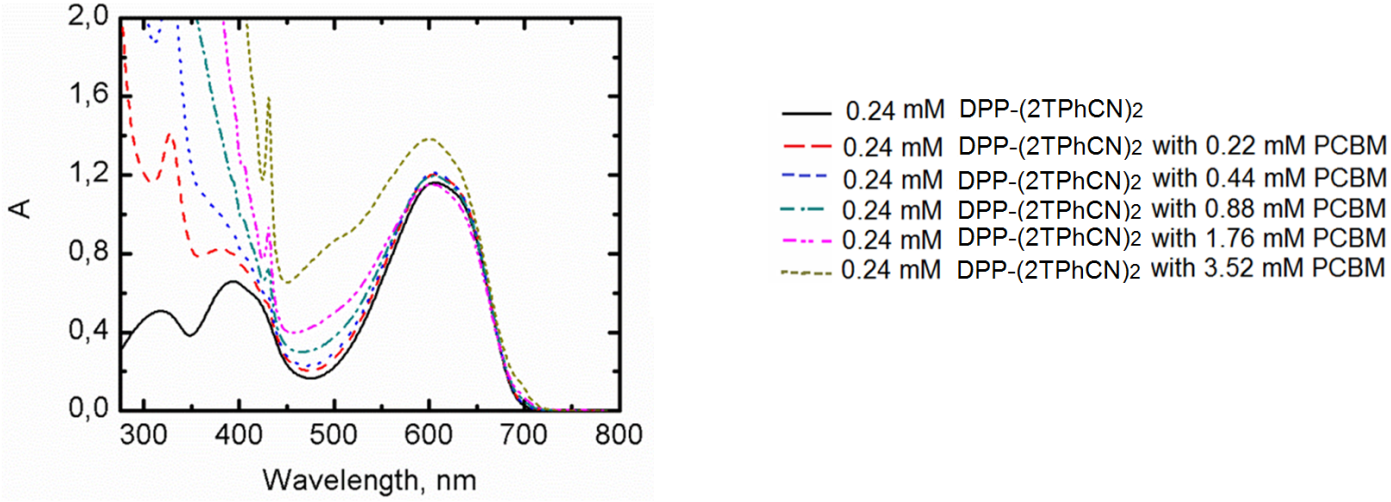


Fig. S5 Absorption spectra of 0.24 mM **DPP-(2TPhCN)$_2$** with different concentrations of PC$_{60}$BM in chloroform.

Solution studies of P3HT and DPP-(2TPhCN)$_2$ interaction

Results of the steady state absorption and emission measurements of P3HT and **DPP-(2TPhCN)$_2$** interaction are shown in Fig. S6 and S7. Fig. S7 shows, that the emission of P3HT is quenched in the presence of **DPP-(2TPhCN)$_2$** molecules in the wavelength range from 525 nm to 675 nm, where the dopant molecules have their absorption band as shown in Fig. S6. The quenching of P3HT emission is most probably due to absorption of the dopant molecules in the solution. If FRET would take place from P3HT to the dopant molecules, the emission of the dopant molecules should be increased at the wavelength range of 700 nm to 850 nm much more than it does in in Fig. S7.

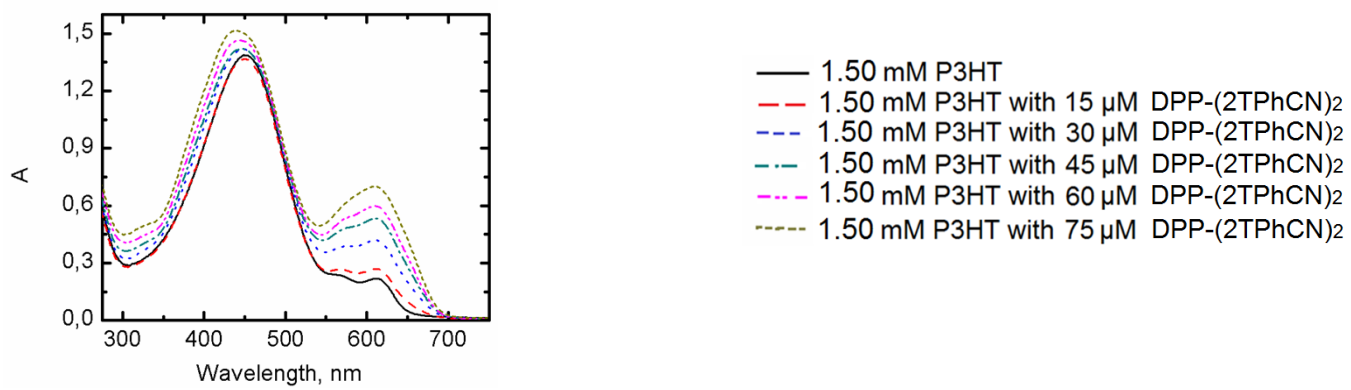


Fig. S6 Absorption spectra of 1.50 mM P3HT with different concentrations of **DPP-(2TPhCN)$_2$** in $CHCl_3$.

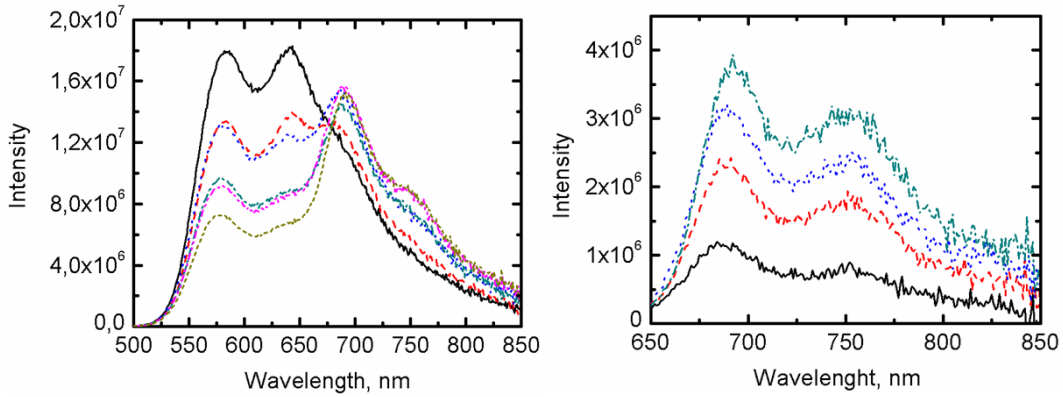


Fig. S7 Emission spectra (left) of 1.50 mM PHT with different concentrations of **DPP-(2TPhCN)$_2$**and emission spectra (right) of 15 µM (black solid), 30 µM (red dashed), 45 µM (blue dotted) and 60 µM (green dash-dotted) **DPP-(2TPhCN)$_2$** in $CHCl_3$.

TCSPC measurements of P3HT and DPP-(2TPhCN)$_2$ interaction

Emission intensity is quenched at 575 nm (Fig. S8, left), as shown by the steady state measurements on page 19. Since the emission lifetime is not decreased, as it should be in the case of FRET, the decrease in the emission intensity is most probably due to absorption of the dopant molecules. If the emission of P3HT at 575 nm is really quenched (which is quite hard to estimate from the emission spectra in Fig. S7), a static quenching, via electron transfer in a molecular complex of P3HT and **DPP-(2TPhCN)$_2$** molecules, is possible. An indication of the formation of the molecular complex could be the lifetimes of the two-exponential fits (of the curves in Fig. S8 (right)) shown in Table S5, since the lifetimes do not correspond to the lifetimes of either P3HT (0.48 ns) or **DPP-(2TPhCN)$_2$** (1.08 ns).

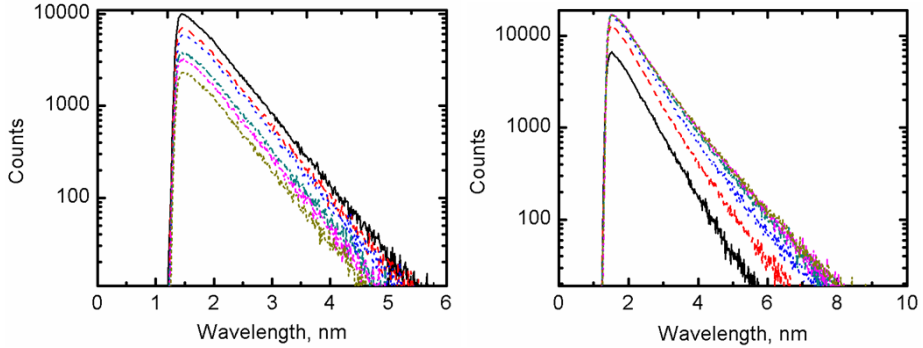


Fig. S8 Emission decay curves (λ_{ex} = 483 nm) of P3HT with different amounts of **DPP-(2TPhCN)$_2$** monitoring at 575 nm (left) and 690 nm (right).

Table S5 Emission lifetimes (λ_{ex} = 483 nm) of P3HT with different concentrations of **DPP-(2TPhCN)$_2$**.

***c*(P3HT)**	***c*(DPP-(2TPhCN)$_2$)**	λ_{mon}	τ_1	τ_2
1.50 mM	-	575 nm	0.48 ns	-
1.50 mM	15 µM	575 nm	0.48 ns	-
1.50 mM	30 µM	575 nm	0.48 ns	-
1.50 mM	45 µM	575 nm	0.48 ns	-
1.50 mM	60 µM	575 nm	0.48 ns	-
1.50 mM	75 µM	575 nm	0.48 ns	-
1.50 mM	-	690 nm	0.60 ns	-
1.50 mM	15 µM	690 nm	0.14 ns	0.72 ns
1.50 mM	30 µM	690 nm	0.17 ns	0.80 ns
1.50 mM	45 µM	690 nm	0.22 ns	0.87 ns
1.50 mM	60 µM	690 nm	0.28 ns	0.92 ns
1.50 mM	75 µM	690 nm	0.30 ns	0.94 ns

Interaction of di-(*p*-CNPh)T4 with P3HT in $CHCl_3$

As shown by the emission spectra in Fig. S9 (right), emission of **di-(*p*-CNPh)T4** is quenched in the presence of P3HT in concentrations from 0.38 mM to 1.52 mM. However, the position of the emission peaks is not shifted to the longer wavelengths, where P3HT emits. Therefore the quenching is not due to energy transfer and electron transfer from **di-(*p*-CNPh)T4** to P3HT is possible. Also, the fluorescence lifetimes do not significantly change in the presence of P3HT (Table S6), which also supports electron transfer as possible mechanism for the **di-(*p*-CNPh)T4** emission quenching.

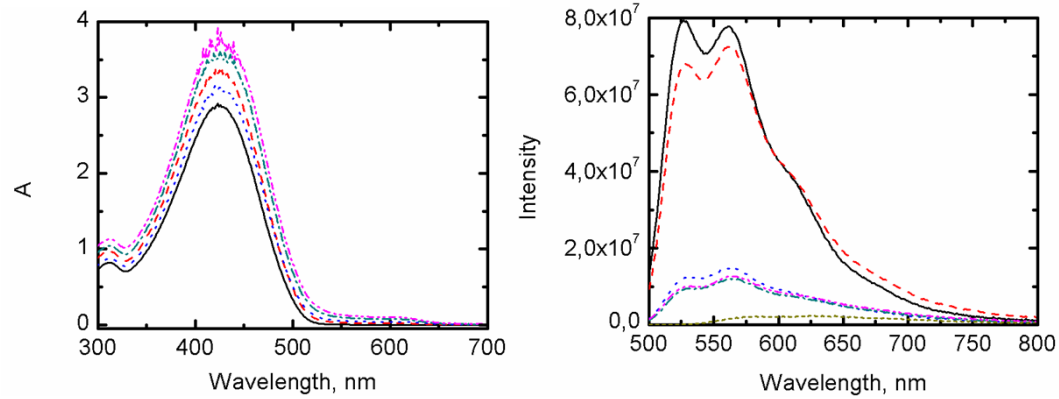
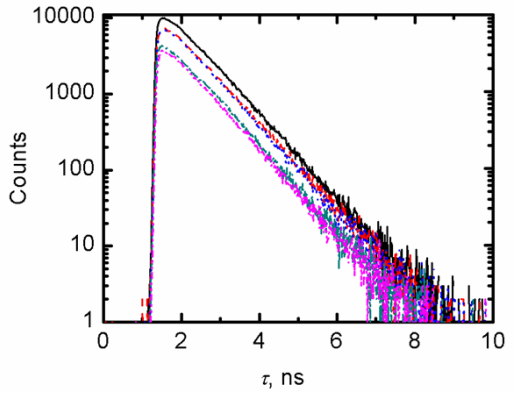


Fig. S9 Absorption (left) and fluorescence emission spectra (λ_{ex} = 483 nm, right) of 0.6 mM **di-(*p*-CNPh)T4** with different concentrations of P3HT in $CHCl_3$.



Samples:

0.6 mM **di-(*p*-CNPh)T4** (black solid)
0.6 mM **di-(*p*-CNPh)T4** and 0.19 mM P3HT (red dash)
0.6 mM **di-(*p*-CNPh)T4** and 0.38 mM P3HT (blue dot)
0.6 mM **di-(*p*-CNPh)T4** and 0.76 mM P3HT (green dash-dot)
0.6 mM **di-(*p*-CNPh)T4** and 1.52 mM P3HT (pink dash-dot-dot)
0.19 mM P3HT (olive short dash, only emission intensity)

Fig. S10 Fluorescence emission decay curves of 0.6 mM **di-(*p*-CNPh)T4** with different concentrations of P3HT in $CHCl_3$ (λ_{ex} = 483 nm).

Table S6 Lifetimes of 0.6 mM **di-(*p*-CNPh)T4** with different concentrations of P3HT in $CHCl_3$.

[di-(*p*-CNPh)T4)] mM	**[P3HT] mM**	**τ (ns)**
0.60	-	0.76
0.60	0.19	0.75
0.60	0.38	0.74
0.60	0.76	0.74
0.60	1.52	0.73

The errors of the lifetimes of the pump-probe fits are shown below in the round brackets after the lifetimes.

DPP-(2TPhCN)$_2$:

VIS: t_1 (lifetime, [t]) =590.559 (0.34869), t_2 (lifetime, [t]) =6.2293 (0.0212413)

NIR: t_1 (lifetime, [t]) =741.985 (0.133345), t_2 (lifetime, [t]) =9.77416 (0.0309011)

DPP-(2TPhCN)$_2$ with PC$_{60}$BM:

VIS: t_1 (lifetime, [t]) =527.925 (0.622699), t_2 (lifetime, [t]) =5.45605 (0.0290579)

NIR: t_1 (lifetime, [t]) =710.923 (15.2163), t_2 (lifetime, [t]) =7.75124 (2.6078)

di-(*p*-CNPh)T4:

VIS: t_1 (lifetime, [t]) =707.493 (137.829), t_2 (lifetime, [t]) =1.01807 (0.474548)

NIR: t_1 (lifetime, [t]) =923.749 (0.564026), t_2 (lifetime, [t]) =5.06717 (0.021506)

di-(*p*-CNPh)T4 with PC$_{60}$BM:

VIS: t_1 (lifetime, [t]) =528.743 (1.00), t_2 (lifetime, [t]) =1.14191 (0.001)

NIR: t_1 (lifetime, [t]) =806.943 (0.349383), t_2 (lifetime, [t]) =3.35264 (0.0123194)