SUPPORTING INFORMATION

Spectroscopic study of a synthesized Alq$_3$ end-capped oligothiophene applied in organic solar cells

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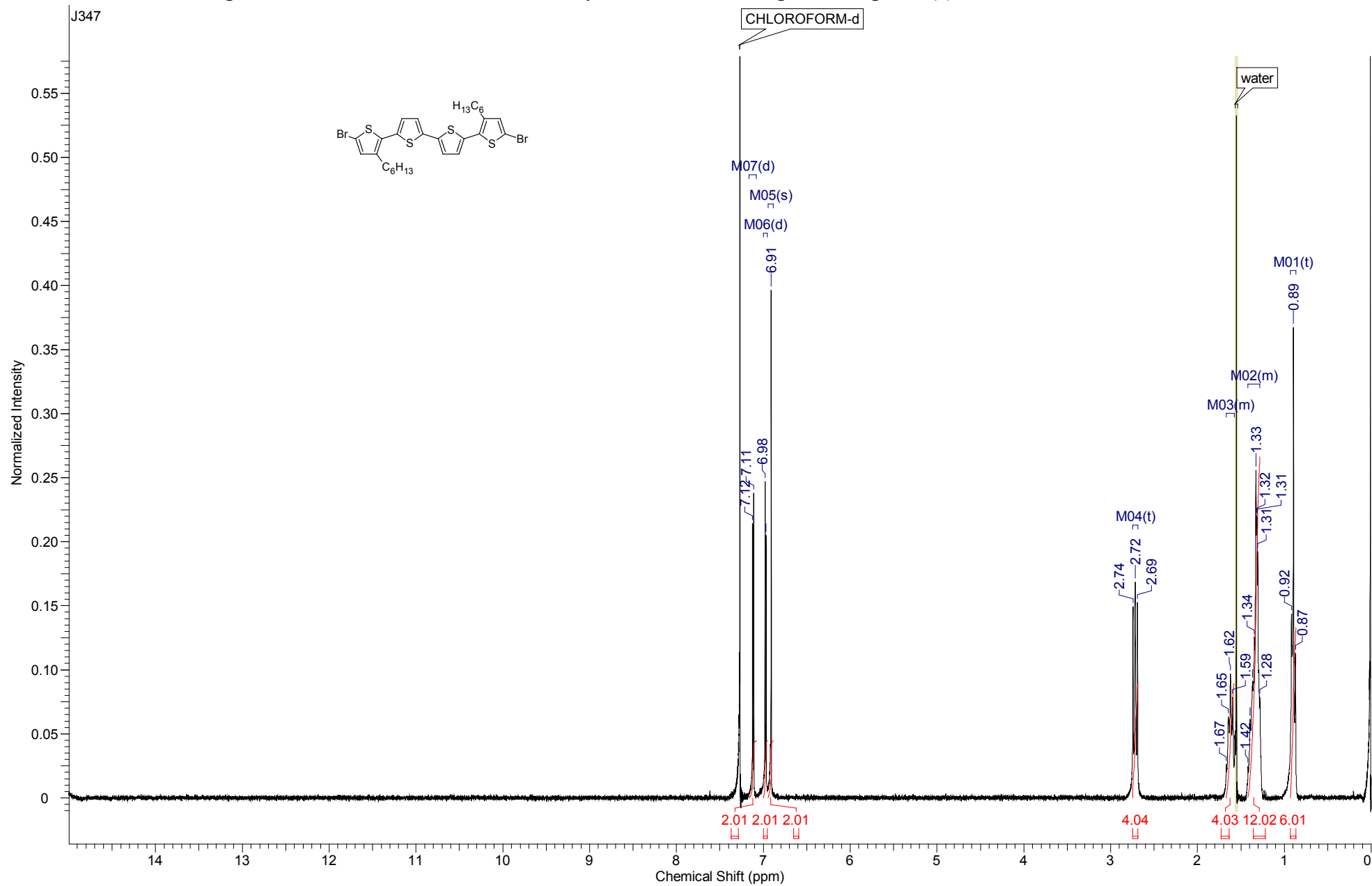
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Contents:

^{1}H NMR spectrum of 5,5'''-dibromo-3,3'''-dihexyl-2,2':5',2'':5'',2'''-quaterthiophene(2)

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No.	Shift1 (ppm)	H's	Type	J (Hz)	Multiplet1	Connections	(ppm)
1	0.89	6	t	6.60	M01	-	[0.87 .. 0.93]
2	1.34	12	m	-	M02	-	[1.28 .. 1.42]
3	1.63	4	m	-	M03	-	[1.58 .. 1.67]
4	2.72	4	t	7.50	M04	-	[2.69 .. 2.75]
5	6.91	2	s	-	M05	-	[6.89 .. 6.95]
6	6.97	2	d	3.93	M06	M07	[6.96 .. 7.00]
7	7.12	2	d	3.93	M07	M06	[7.08 .. 7.16]

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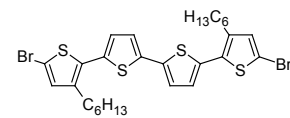
^{1}H NMR spectrum of 3,3'''',3''''',4'-tetrahexyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2'''''-sexithiophene(3)
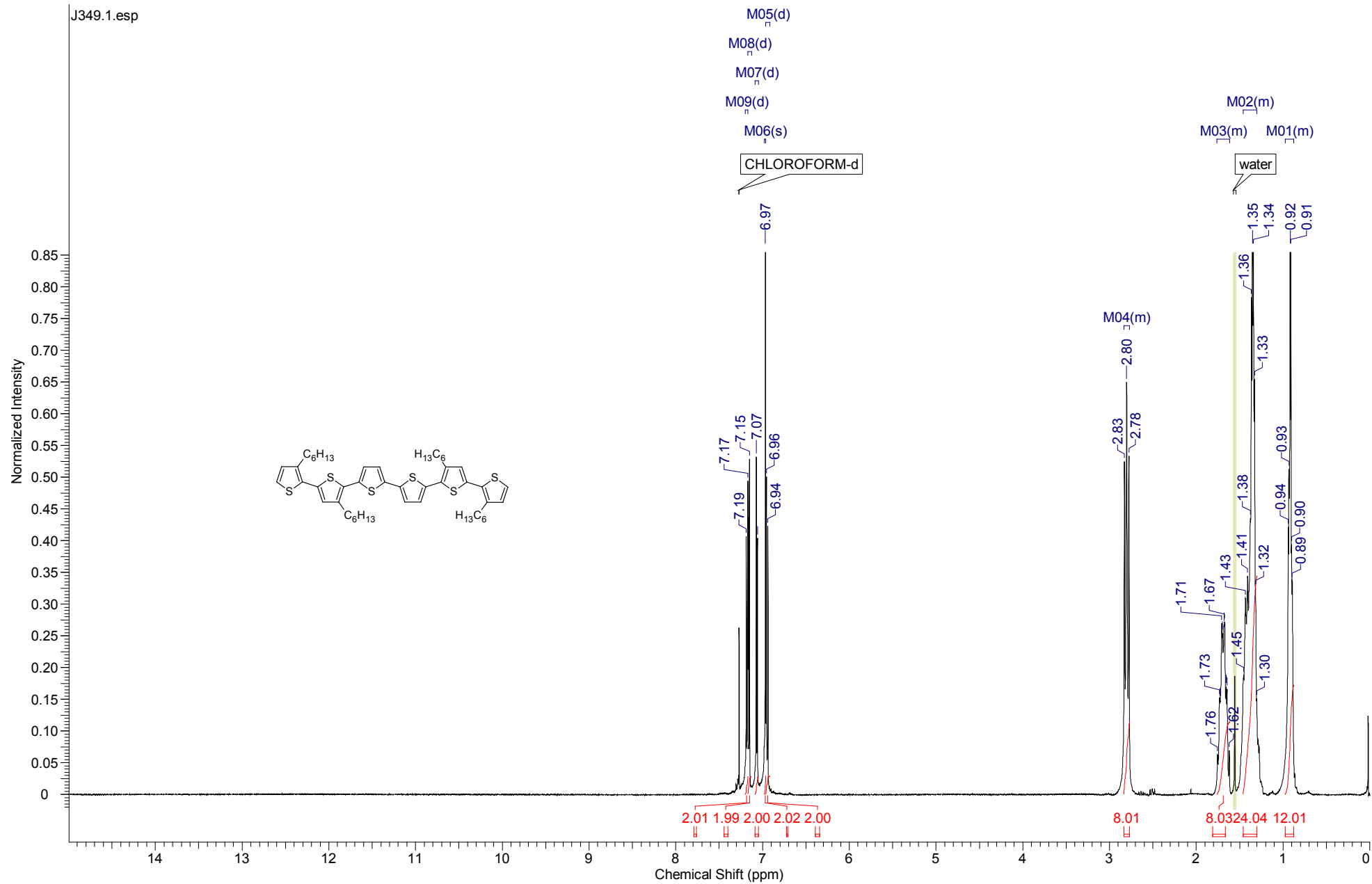
No.	Shift1 (ppm)	H's	Type	J (Hz)	Multiplet1	Connections	(ppm)
1	0.92	12	m	-	M01	-	[0.88 .. 0.97]
2	1.37	24	m	-	M02	-	[1.30 .. 1.46]
3	1.69	8	m	-	M03	-	[1.61 .. 1.76]
4	2.80	8	m	-	M04	-	[2.77 .. 2.84]
5	6.95	2	d	5.20	M05	M09	[6.92 .. 6.96]
6	6.97	2	s	-	M06	-	[6.96 .. 6.98]
7	7.07	2	d	3.74	M07	M08	[7.05 .. 7.09]
8	7.16	2	d	3.74	M08	M07	[7.13 .. 7.17]
9	7.18	2	d	5.20	M09	M05	[7.17 .. 7.20]

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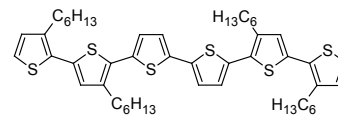
^{1}H NMR spectrum of 5,5'''''-dibromo-3,3'''',3''''',4'-tetrahexyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2'''''-sexithiophene(4)
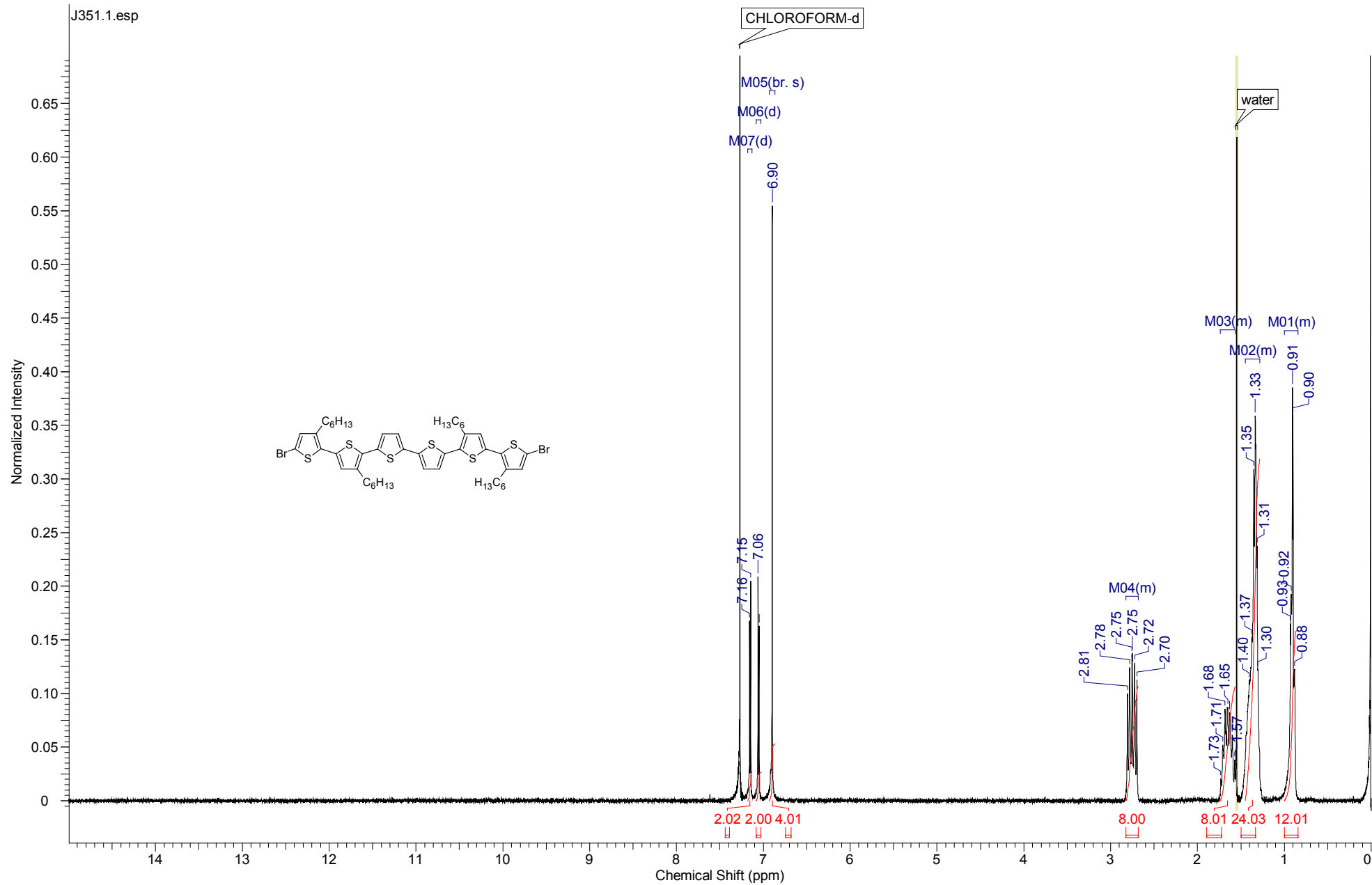
No.	Shift1 (ppm)	H's	Type	J (Hz)	Multiplet1	Connections	(ppm)
1	0.91	12	m	-	M01	-	[0.84 .. 1.00]
2	1.35	24	m	-	M02	-	[1.28 .. 1.45]
3	1.65	8	m	-	M03	-	[1.57 .. 1.74]
4	2.75	8	m	-	M04	-	[2.68 .. 2.82]
5	6.90	4	br. s	-	M05	-	[6.87 .. 6.93]
6	7.05	2	d	3.74	M06	M07	[7.03 .. 7.08]
7	7.15	2	d	3.74	M07	M06	[7.13 .. 7.18]
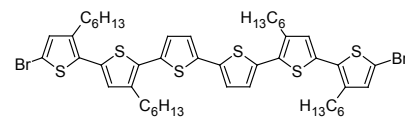
^{1}H NMR spectrum of 5,5'-(3,3'''',3'''''',4'-tetrahexyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2''''''-sexithiene-5,5'''''-diyl)bis[8-(benzyloxy)quinoline] (5)
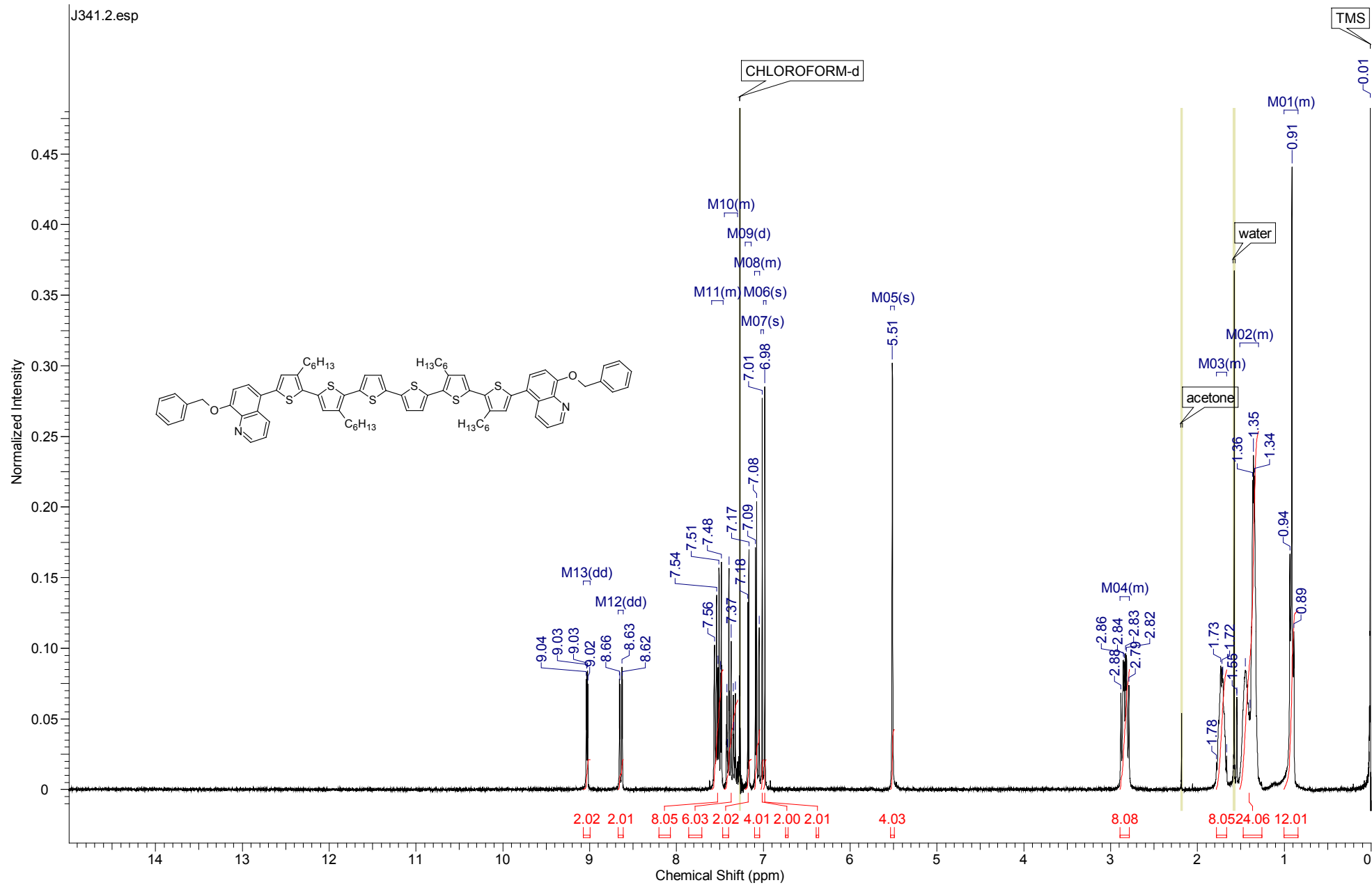
No.	Shift1 (ppm)	H's	Type	J (Hz)	Multiplet1	Connections	(ppm)
1	0.91	12	m	-	M01	-	[0.84 .. 1.01]
2	1.38	24	m	-	M02	-	[1.29 .. 1.51]
3	1.72	8	m	-	M03	-	[1.66 .. 1.78]
4	2.84	8	m	-	M04	-	[2.78 .. 2.89]
5	5.51	4	s	-	M05	-	[5.49 .. 5.54]
6	6.98	2	s	-	M06	-	[6.97 .. 7.00]
7	7.01	2	s	-	M07	-	[7.00 .. 7.03]
8	7.07	4	m	-	M08	-	[7.04 .. 7.10]
9	7.17	2	d	3.74	M09	M13	[7.14 .. 7.21]
10	7.38	6	m	-	M10	-	[7.29 .. 7.45]
11	7.52	8	m	-	M11	-	[7.46 .. 7.60]
12	8.64	2	dd	8.56, 1.71	M12	?, M13	[8.61 .. 8.67]
13	9.03	2	dd	4.20, 1.71	M13	M09, M12	[8.99 .. 9.07]

^{13}C NMR spectrum of 5,5'-(3,3'''',3''''',4'-tetrahexyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2''''''-sexithiene-5,5'''''-diyl)bis[8-(benzyloxy)quinoline] (5)
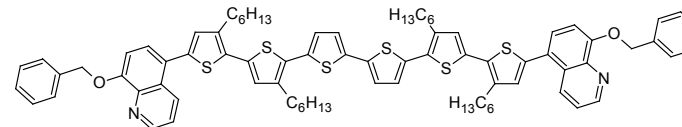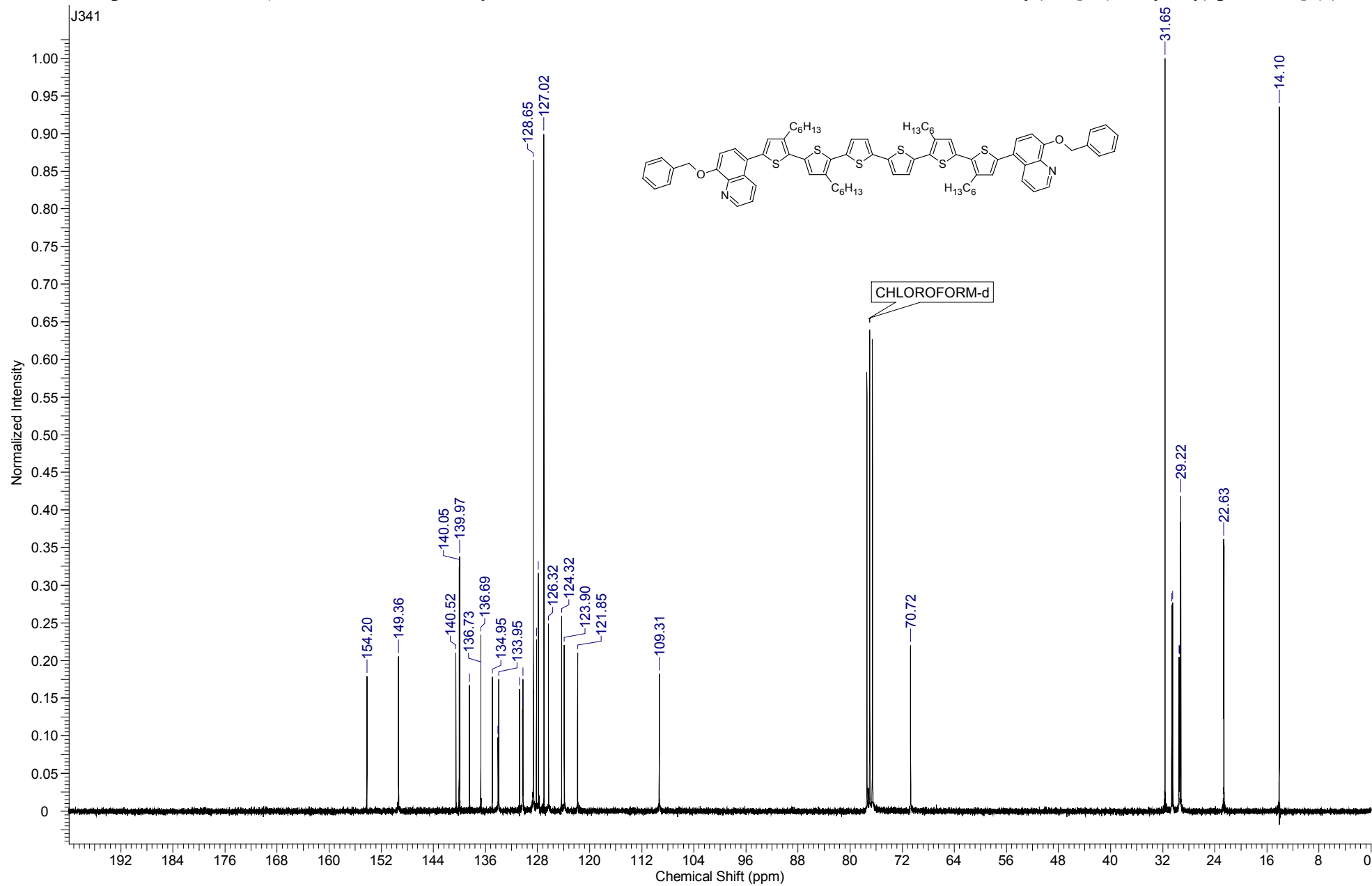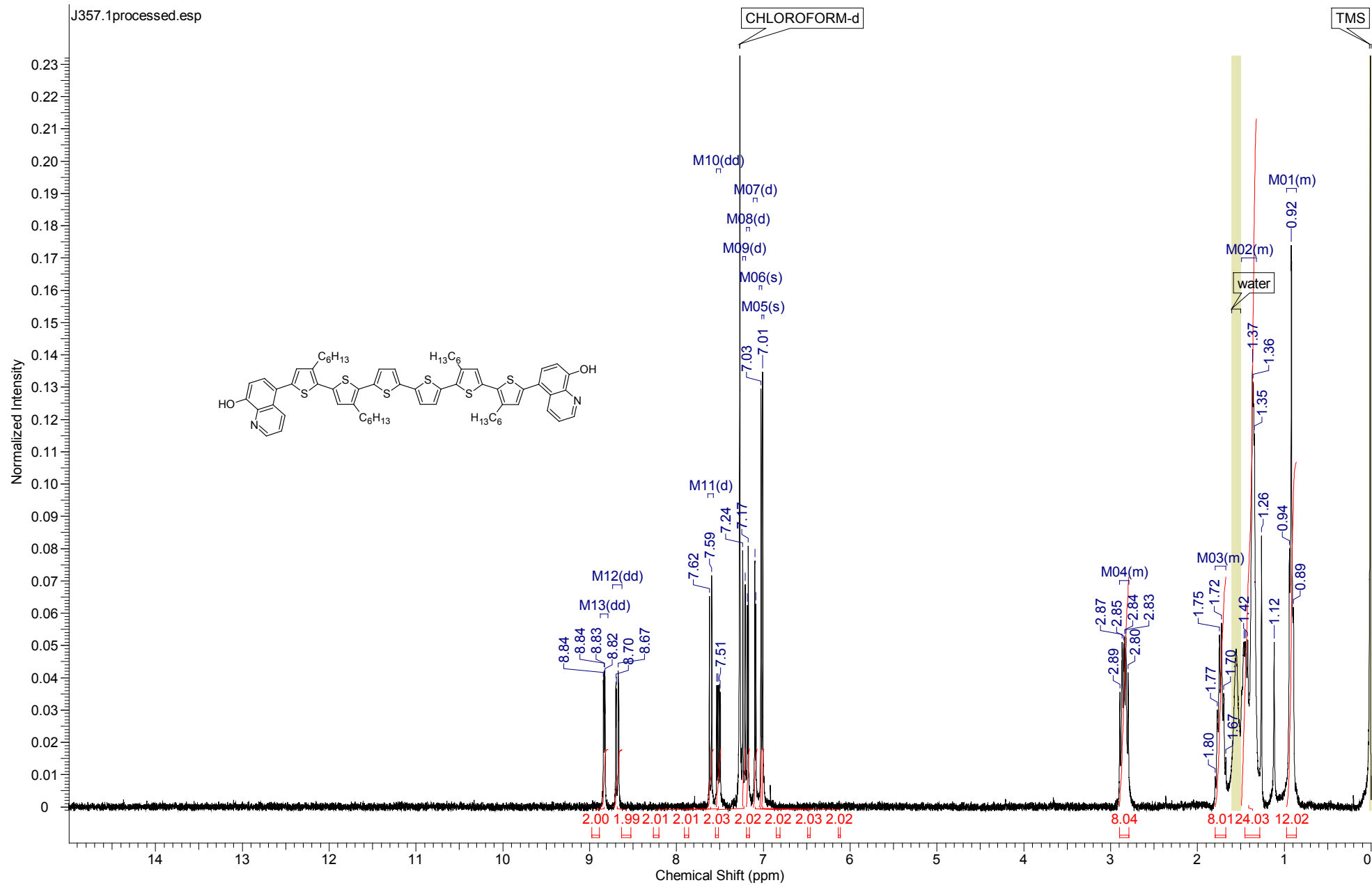
No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	14.10	1063.5	0.9356	9	30.62	2309.7	0.2738	17	127.02	9580.5	0.8994	25	130.77	9863.1	0.1619	33	140.05	10563.5	0.3239
2	22.60	1704.9	0.3526	10	31.65	2387.1	1.0000	18	127.83	9641.9	0.2145	26	133.95	10103.0	0.1752	34	140.52	10598.9	0.2106
3	22.63	1707.1	0.3611	11	70.72	5333.9	0.2202	19	127.86	9644.1	0.3161	27	134.07	10112.4	0.0981	35	149.36	11265.1	0.2055
4	29.22	2203.6	0.4188	12	109.31	8244.8	0.1821	20	128.18	9667.9	0.2280	28	134.95	10178.7	0.1786	36	154.20	11630.6	0.1788
5	29.27	2207.4	0.3843	13	121.85	9190.8	0.2106	21	128.63	9702.2	0.1611	29	136.69	10309.8	0.2343				
6	29.43	2219.6	0.2040	14	123.90	9345.0	0.2203	22	128.65	9703.8	0.8644	30	136.73	10312.5	0.1880				
7	29.52	2226.8	0.2049	15	124.32	9376.5	0.2591	23	130.23	9822.7	0.1747	31	138.45	10442.5	0.1671				
8	30.47	2298.1	0.2766	16	126.32	9527.5	0.2485	24	130.29	9827.1	0.1351	32	139.97	10557.5	0.3379				
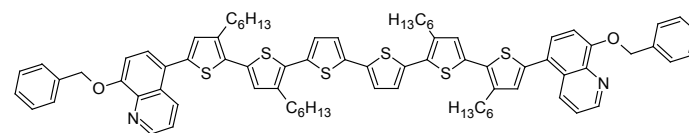
^{1}H NMR spectrum of 5,5'-(3,3'''',3''''',4'-tetrahexyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2'''''-sexithiene-5,5'''''-diyl)diquinolin-8-ol (6)

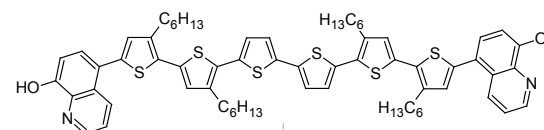| No. | Shift1 (ppm) | H's | Type | J (Hz) | Multiplet1 | Connections | (ppm) | No. | Shift1 (ppm) | H's | Type | J (Hz) | Multiplet1 | Connections | (ppm) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.92 | 12 | m | - | M01 | - | [0.86 .. 0.97] | 8 | 7.18 | 2 | d | 3.74 | M08 | M07 | [7.16 .. 7.20] |
| 2 | 1.40 | 24 | m | - | M02 | - | [1.32 .. 1.49] | 9 | 7.22 | 2 | d | 7.90 | M09 | M11 | [7.21 .. 7.24] |
| 3 | 1.73 | 8 | m | - | M03 | - | [1.67 .. 1.80] | 10 | 7.52 | 2 | dd | 8.60, 4.20 | M10 | M12, M13 | [7.49 .. 7.54] |
| 4 | 2.85 | 8 | m | - | M04 | - | [2.79 .. 2.90] | 11 | 7.61 | 2 | d | 7.90 | M11 | M09 | [7.58 .. 7.64] |
| 5 | 7.01 | 2 | s | - | M05 | - | [7.00 .. 7.02] | 12 | 8.68 | 2 | dd | 8.60, 1.60 | M12 | M10, M13 | [8.63 .. 8.74] |
| 6 | 7.03 | 2 | s | - | M06 | - | [7.02 .. 7.05] | 13 | 8.83 | 2 | dd | 4.20, 1.60 | M13 | M10, M12 | [8.79 .. 8.88] |
| 7 | 7.09 | 2 | d | 3.74 | M07 | M08 | [7.07 .. 7.11] | | | | | | | | |

^{13}C NMR spectrum of 5,5'-(3,3''',3'''''',4'-tetrahexyl-2,2':5',2'':5'',2''':5''',2'''':5'''',2''''''-sexithiene-5,5'''''-diyl)diquinolin-8-ol (6)
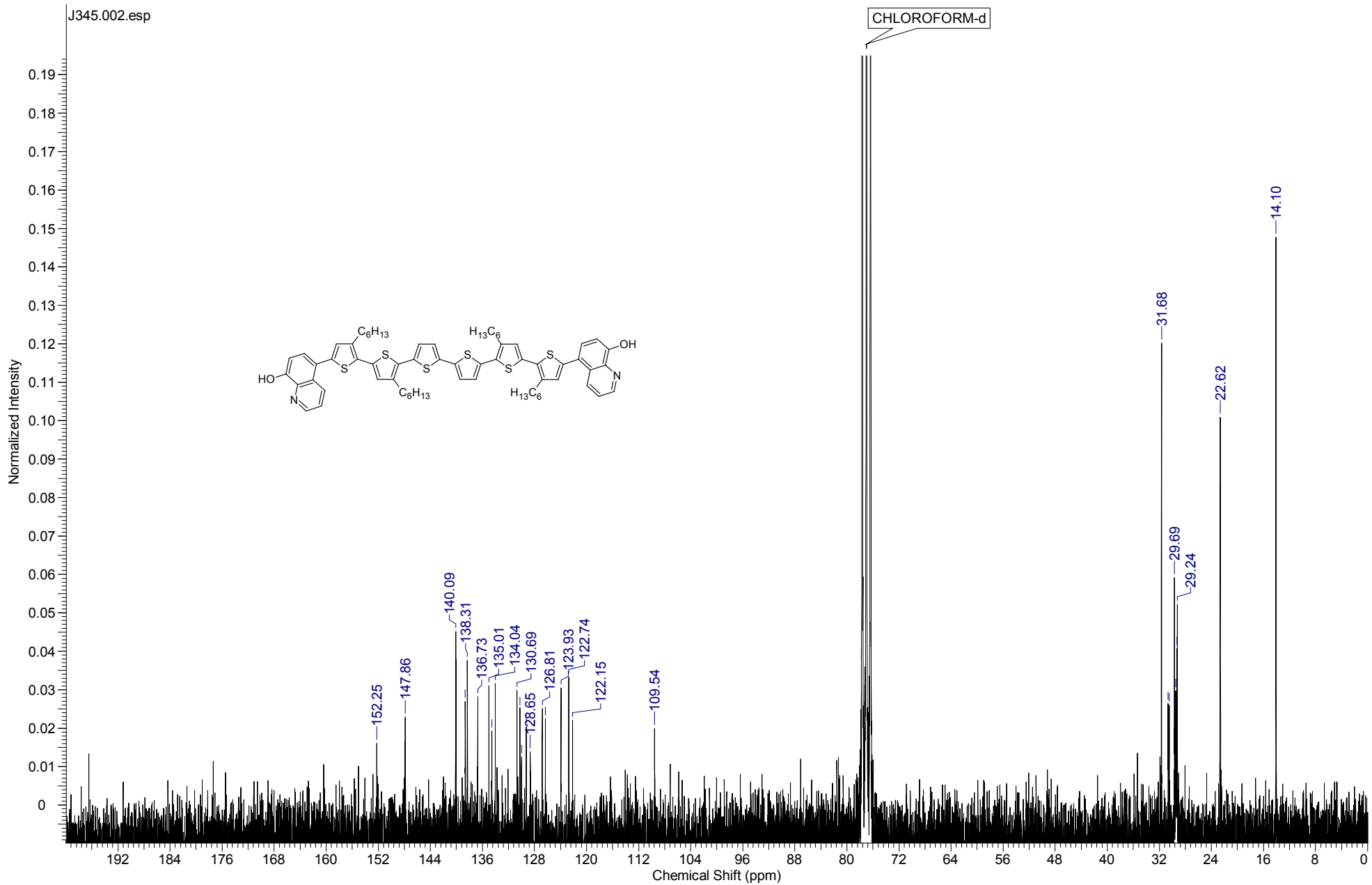

J345.002.esp

CHLOROFORM-d

Normalized Intensity

Chemical Shift (ppm)

Peaks: 152.25, 147.86, 140.09, 138.31, 136.73, 135.01, 134.04, 130.69, 128.65, 126.81, 123.93, 122.74, 122.15, 109.54, 31.68, 29.69, 29.24, 22.62, 14.10

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| No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height	No.	(ppm)	(Hz)	Height
1	14.10	709.8	0.1478	8	29.69	1494.0	0.0592	15	123.93	6236.3	0.0306	22	130.69	6576.7	0.0299	29	140.04	7047.3	0.0377
2	22.62	1138.5	0.1010	9	30.49	1534.3	0.0260	16	126.34	6357.7	0.0225	23	134.04	6745.0	0.0316	30	140.09	7049.5	0.0452
3	22.65	1139.6	0.0832	10	30.66	1543.1	0.0265	17	126.81	6381.5	0.0251	24	134.55	6770.7	0.0193	31	147.86	7440.5	0.0229
4	29.24	1471.2	0.0522	11	31.68	1594.1	0.1202	18	128.65	6474.0	0.0139	25	135.01	6793.8	0.0311	32	152.25	7661.7	0.0161
5	29.31	1474.9	0.0408	12	109.54	5512.2	0.0199	19	129.26	6504.8	0.0204	26	136.73	6880.8	0.0282				
6	29.46	1482.6	0.0297	13	122.15	6146.8	0.0221	20	130.00	6542.2	0.0125	27	138.31	6960.0	0.0376				
7	29.56	1487.7	0.0253	14	122.74	6176.5	0.0332	21	130.23	6553.6	0.0250	28	138.64	6976.5	0.0270				
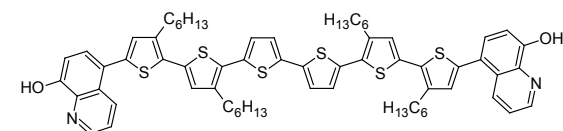
^{1}H NMR spectrum of $(Alq_3)_2$-OT
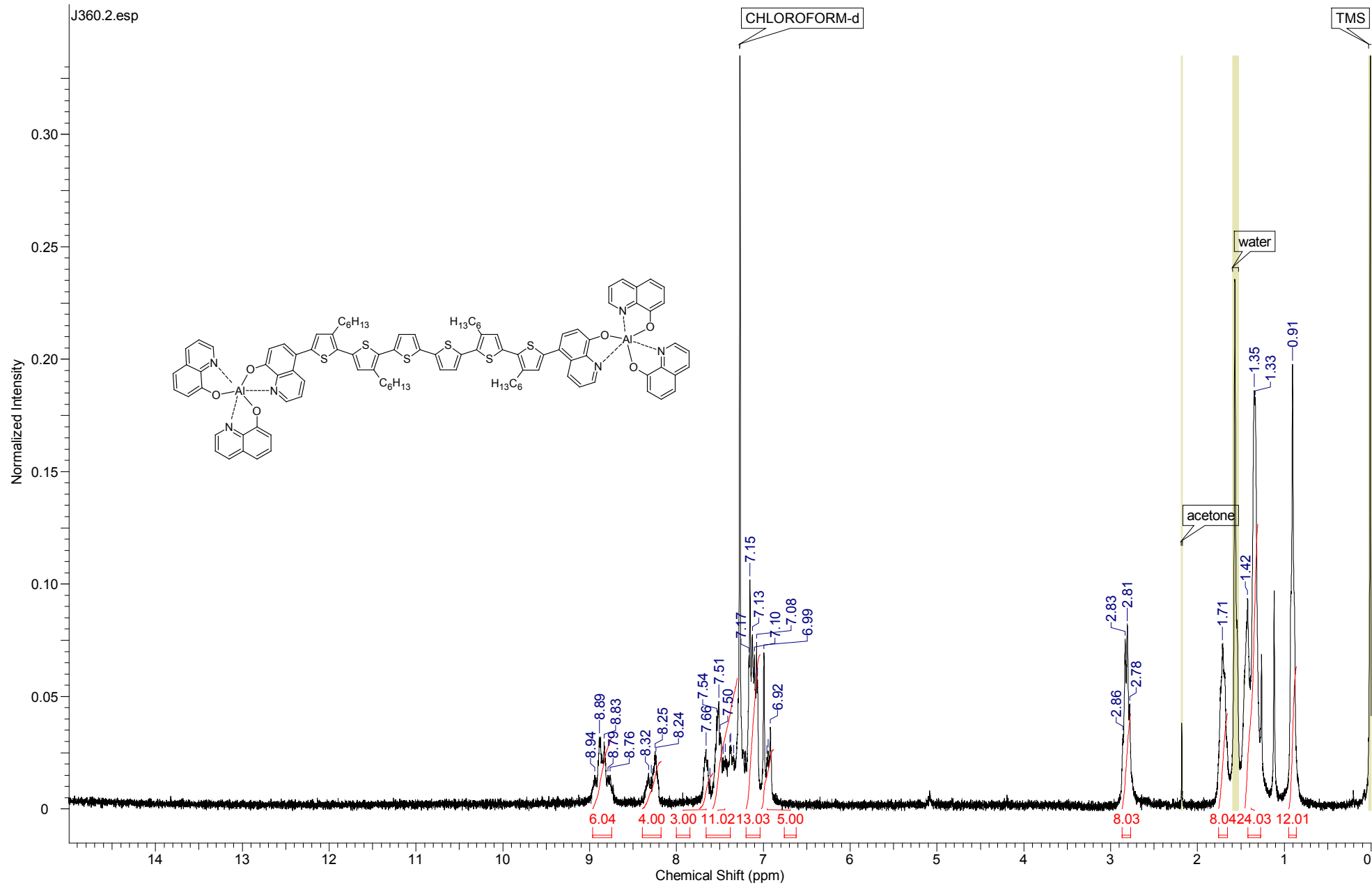
Quenching of compound 5, Alq₃ and (Alq₃)₂-OT and in the presence of PCBM

Quenching via the dissociation of PCBM to compound **5**. Alq$_3$ and (Alq$_3$)$_2$-OT would give values of quenching coefficients (k_q) around 10^{10} s^{-1}. The values of k_q calculated from the intensities of Table 1 (from Figure 3) according to Stern Volmer equation ($\frac{I_{PL}^0}{I_{PL}} = 1 + k_q \tau_0 [Q]$, $I_{PL}{}^0$ = emission intensity without quencher, I_{PL} = emission intensity in the presence of quencher PCBM, τ_0 = lifetime without quencher, [Q] = concentration of the quencher) are larger than 10^{11} s^{-1} for all three compounds. This means that the quenching process does not involve the dissociation of the PCBM molecule. Thus, PCBM is associated with the compounds in the solutions.

## TCSPC decay curves of the (Alq₃)₂-OT and PCBM film samples and DAS spectra of (Alq₃)₂-OT and PCBM in CHCl₃
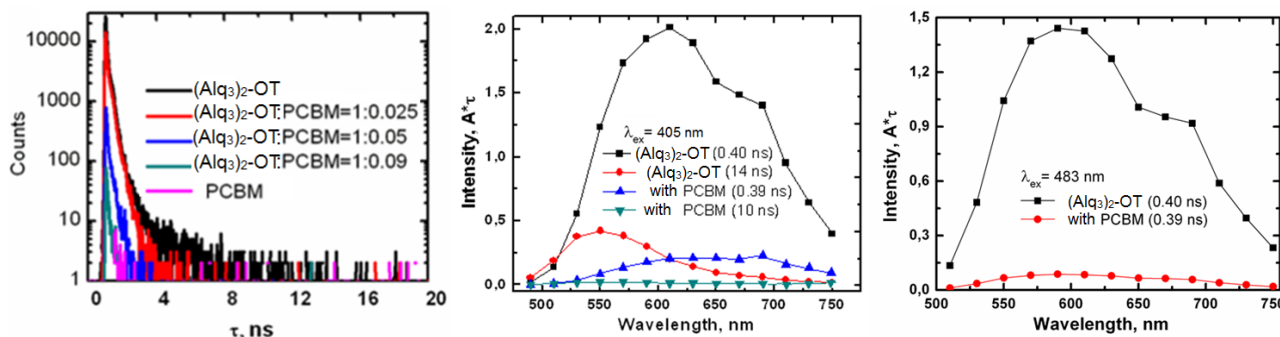
Figure S1. *TCSPC decay curves of the studied (Alq₃)₂-OT and PCBM films (left), DAS of (Alq₃)₂-OT (0.22 mM) and mixture of (Alq₃)₂-OT (0.22 mM) and PCBM (0.84 mM) in CHCl₃ with excitation wavelengths 405 nm (center) and 483 nm (right).*

Table of the solar cell results with compound 5

Table S1. *Photovoltaic parameters of the cells with compound **5** as an additional compound in the active layer.*

Cell structure Mass ratio of the components	$J_{sc,best}$ (mA/cm^2)	$V_{oc, best}$ (V)	FF $_{best}$ (%)	η_{best} (%)	η_{avg} (%)
ITO|ZnO|**PHT:PCBM**|Alq₃|Au 9.0 mg : 7.1 mg (DCB)	-3.40	0.53	60.26	**2.94**	2.58
ITO|ZnO|**PHT:PCBM:5**|Alq₃|Au 8.8 mg : 7.2 mg : 1.8 mg (DCB)	-3.19	0.50	59.82	**2.57**	2.18
ITO|ZnO|**PHT:PCBM:5**| Alq₃|Au 8.8 mg : 7.2 mg : 1.8 mg (DCB, CHCl₃)	-3.79	0.50	55.11	**2.82**	2.44
ITO|ZnO|**PHT:PCBM:5**| Alq₃|Au 9.1 mg : 7.0 mg : 2.7 mg (DCB)	-3.01	0.51	56.31	**2.34**	2.13

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Absorption and emission spectra of the evaporated films of $(Alq_3)_2$-OT
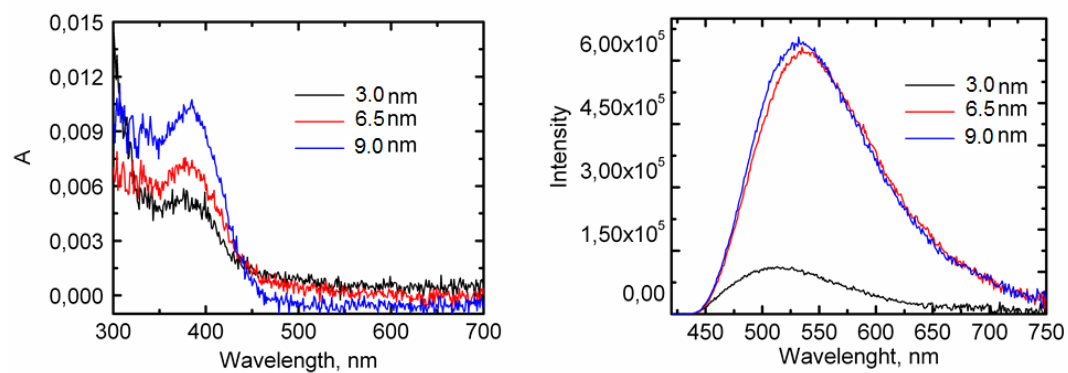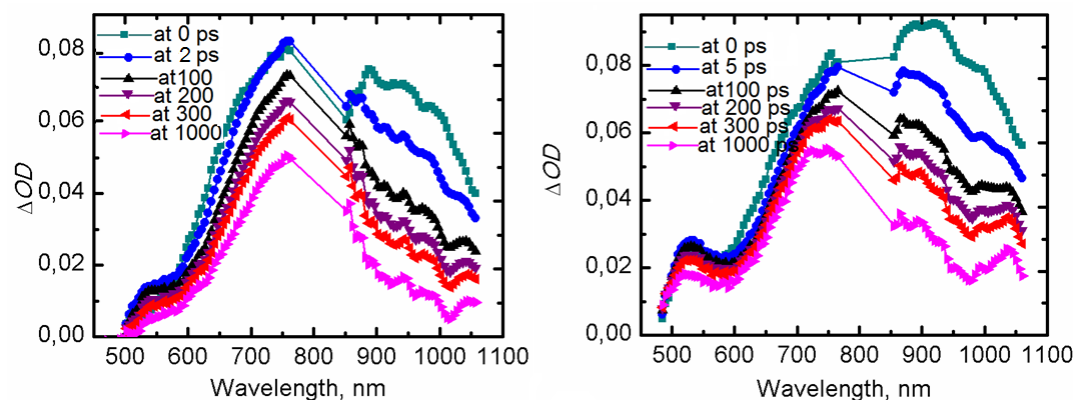

Figure S2. *Absorption and emission spectra of the thermally evaporated (185 – 285 °C) 3 nm, 6.5 nm and 9.0 nm films of $(Alq_3)_2$-OT.*

DSC curve of $(Alq_3)_2$-OT
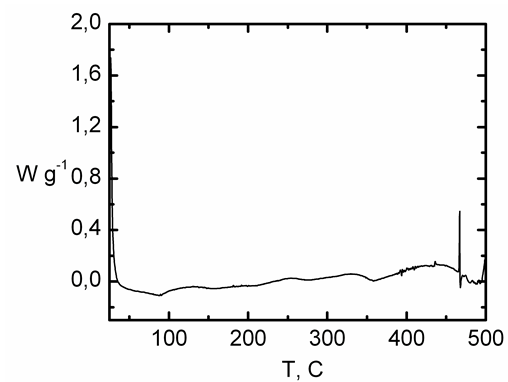
Figure S3. *Differential scanning calorimetry curve of the $(Alq_3)_2$-OT. Thermal decomposition takes place around 400 °C.*

Transient absorption and decay component spectra of the $(Alq_3)_2$-OT in the absence and presence of PCBM

Figure S4. Transient absorption spectra of the $(Alq_3)_2$-OT (0.22 mM) in the absence (left) and in the presence (right) of PCBM (0.84 mM) at 0 ps, 5 ps, 100 ps, 200 ps, 300 ps and 1000 ps after photoexcitation at 390 nm in $CHCl_3$.

Excitation spectra of compound 5 and $(Alq_3)_2$-OT

The excitation spectra of compound **5** and $(Alq_3)_2$-OT in Figure S5 show that the excitation spectrum maxima of $(Alq_3)_2$-OT and compound **5** are at 401 nm and 417 nm, respectively. Absorption spectra of the compounds overlap, but the excitation spectrum maximum of $(Alq_3)_2$-OT is blue shifted compared to that of compound **5**. Emission of the oligothiophene moiety is partly quenched due to the intramolecular electron transfer from the oligothiophene backbone to the Alq_3 moieties in $(Alq_3)_2$-OT and the emission maximum of $(Alq_3)_2$-OT shifts towards Alq_3 emission maximum.
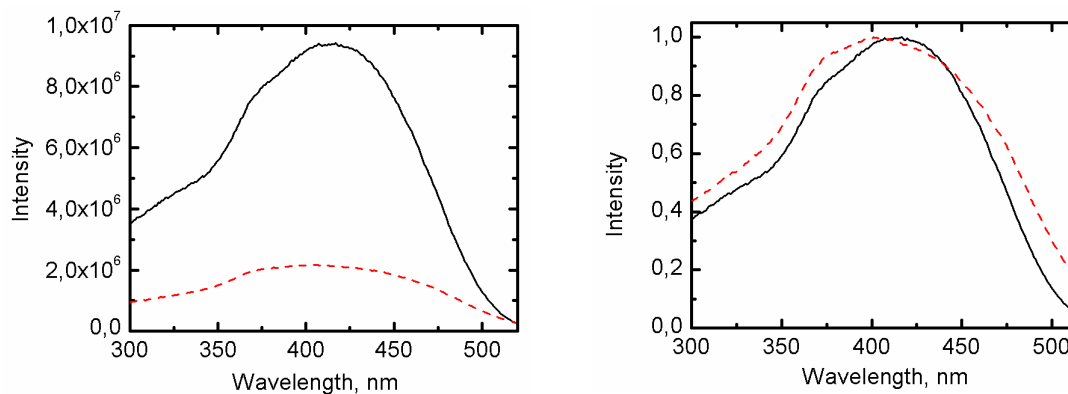
Figure S5. Excitation (left) and normalized excitation spectra (right) of 0.22 mM $(Alq_3)_2$-OT (dashed line) and compound **5** (solid line) in $CHCl_3$ monitoring at 550 nm and exciting from 300 nm to 520 nm.

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DPV curves of compound 5 and (Alq$_3$)$_2$-OT and calculations of the HOMO and LUMO levels

Energy levels of (Alq$_3$)$_2$-OT

The peak potential of (Alq$_3$)$_2$-OT in the backward (negative) scan is -2.103 V for calculating the LUMO level (Figure S6, left, red line). The corresponding reduction peak in the forward (positive) scan can be seen as a vague shoulder. The oxidation peak potential of the forward scan is 0.608 V and the corresponding peak value of the backward scan is 0.610 V. Therefore, the half wave potential (V$_{1/2}$) for calculating the HOMO level is 0.609 V ([0.608 V + 0.610 V] / 2). Ferrocene reference peak potentials appear at 0.230 V and 0.205 V in the forward and backward scans, respectively (Figure S6, left, black line). V$_{1/2}$ of ferrocene used for the energy level calculations is 0.2175 V ([0.230 V + 0.205 V] / 2).

HOMO and LUMO level calculations were based on the formal oxidation and reduction potentials observed in the DPV curves according to the following equations:

$$E_{HOMO} = - (4.8 + E_{dif,ox}) \text{ eV} = - (4.8 + [0.609 - 0.2175]) \text{ eV} = -5.1915 \text{ eV} \approx -5.2 \text{ eV}$$
$$E_{LUMO} = (-E_{dif,red} + 4.8) \text{ eV} = (-[2.103 + 0.2175] + 4.8) \text{ eV} = -2.4795 \text{ eV} \approx -2.5 \text{ eV}$$

where 4.8 eV is the oxidation energy of ferrocene. $E_{dif,ox}$ is the difference in volts between the formal oxidation potentials of ferrocene and the measured sample. $E_{dif,red}$ is the difference in volts between the formal oxidation potential of ferrocene and the formal reduction potential of the sample.

Energy levels of compound 5

The peak potential of compound **5** reduction in the forward scan can be seen as a shoulder at -2.25 V and the corresponding shoulder value of the backward scan is -2.30 V (Figure S6, right, red curve). V$_{1/2}$ of compound **5** for calculating the LUMO level is -2.275 V ([-2.25 V + -2.30] / 2). The peak around -1.5 V in the backward scan is due to some impurity. The oxidation peak potential of the forward scan is 0.58 V and the corresponding peak value of the backward scan is 0.62 V. V$_{1/2}$ of compound **5** for calculating the HOMO level is 0.60V ([0.58 V + 0.62 V] / 2). Ferrocene reference peak potentials appear at 0.250 V and 0.240 V in the forward and backward scans, respectively (Figure S6, right, black line). V$_{1/2}$ of ferrocene used for the energy level calculations is 0.245 V ([0.250 V + 0.240 V] / 2).

HOMO and LUMO level calculations were based on the formal oxidation and reduction potentials observed in the DPV curves according to the following equations:

$$E_{HOMO} = - (4.8 + E_{dif,ox}) \text{ eV} = - (4.8 + [0.60 - 0.245]) \text{ eV} = -5.155 \text{ eV} \approx -5.2 \text{ eV}$$
$$E_{LUMO} = (-E_{dif,red} + 4.8) \text{ eV} = (-[2.275 + 0.245] + 4.8) \text{ eV} = -2.28 \text{ eV} \approx -2.3 \text{ eV}$$

where 4.8 eV is the oxidation energy of ferrocene. $E_{dif,ox}$ is the difference in volts between the formal oxidation potentials of ferrocene and the measured sample. $E_{dif,red}$ is the difference in volts between the formal oxidation potential of ferrocene and the formal reduction potential of the sample.

In the absence of clear reduction peak of compound **5** (only shoulders appear), LUMO level for the compound is calculated based on the optical band gap. Absorption maximum of the compound appears at 423 nm and the optical band gap is 2.9334 eV. LUMO = HOMO – 2.9334 eV = -5.155 eV – (2.9334 eV) = -2.2216 eV ≈ 2.2 eV.
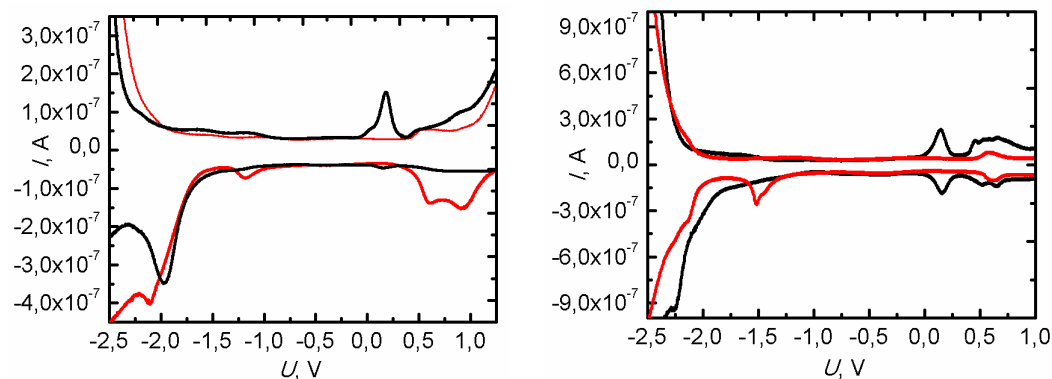
Figure S6. DPV curve of (Alq$_3$)$_2$-OT (left) and compound **5** (right) in the absence (red) and presence (black) of ferrocene reference.