SUPPLEMENTARY INFORMATION

Ultrafast Intramolecular Energy Transfer in Nanostructured Organosilicon Luminophore Based on *p*-Terphenyl and 1,4-bis(5-Phenyloxazol-2-yl)benzene

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CONTENT

1. Experimental section

1.1. Materials

2-Ethylhexyl bromide and 1,4-dibromobenzene were obtained from Acros organics; magnesium and [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) complex with dichloromethane (Pd(dppf)Cl_2) were obtained from Sigma-Aldrich and used as received. 1-Bromo-4-(trimethylsilyl)benzene was obtained by the method described previously.[1] THF and diethyl ether were dried and purified according to the well-known techniques and then used as the solvents. All reactions, unless otherwise stated, were carried out in an inert atmosphere using anhydrous solvents. In the case of column chromatography, silica gel 60Å ("Merck") was taken. For thin layer chromatography, "Sorbfil" (Russia) plates were used.

1.2. Characterization

The ^{1}H NMR spectra were recorded on a "Bruker AC-250" spectrometer (250 MHz) using the residual signal of $CDCl_3$ (δ 7.27 ppm) as the internal standard. The ^{13}C and ^{29}Si NMR spectra were recorded on a Bruker AVII-300 spectrometer at working frequencies 75 MHz and 60 MHz, respectively. In the case of ^{1}H NMR spectroscopy, the compounds to be analyzed were taken in the form of 1% solutions in $CDCl_3$. In the case of ^{13}C or ^{29}Si NMR spectroscopy, the compounds to be analyzed were taken in the form of 3-5% solutions in $CDCl_3$. The spectra were then processed on the computer using the ACD Labs v.10.04 software.

Elemental analysis of C, H, N elements was carried out using CHN automatic analyzer CE1106 (Italy). Experimental error is 0.30−0.50 %. The burning was done in the Sheninger flask using alkaline solution of hydrogen peroxide as an absorbent. For the Si analysis spectrophotometry technique was used.

Mass-spectra (MALDI) were registered on the Autoflex II Bruker (resolution FWHM 18000), equipped with nitrogen laser (work wavelength 337 nm) and time-of-flight mass-detector working in reflections mode. The resulting spectrum was the sum of 300 spectra obtained at different points of sample. 2,5-Dihydroxybenzoic acid (DHB) (Acros, 99%) and α-cyano-4-hydroxycinnamic acid (HCCA) (Acros, 99%) were used as matrices.

Thermogravimetric analysis was carried out in dynamic mode in 30-800 °C interval using Mettler Toledo TG50 system equipped with M3 microbalance allowing measuring the weight of the samples in 1-150 mg range with 1 μg precision. Heating/cooling rate was chosen to be 20 °C/min. Every compound was studied twice: in air and under nitrogen flow of 200 mL/min.

Cyclic voltammetry (CV) measurements were carried out on films rubbed on the electrode in acetonitrile using 0.1 M Bu_4NPF_6 as the supporting electrolyte. The scan rate was 200 mV/s. The glassy carbon electrode was used as a working electrode. A platinum plate was used as the counter electrode. The potentials were measured relative to a saturated calomel electrode (SCE). The standard potentials for quasireversible reduction and irreversible oxidation processes were estimated as $\boldsymbol{\varphi_{red}} = E^{1/2}_{red} = E_{red} + 0.06$ V and $\boldsymbol{\varphi_{ox}} = E^{1/2}_{ox} = E_{ox} - 0.06$ V as reported before [2]. Based on the CV oxidation and reduction potentials, values of the highest occupied molecular orbitals (HOMO), the lowest unoccupied molecular orbitals (LUMO) and the CV bandgap were calculated using the equations 1, 2 and 3 [3]:

$$\mathbf{E}(\text{HOMO}) = -e(\phi_{ox} + 4.40)\ (\text{eV}) \quad (1)$$

$$\mathbf{E}(\text{LUMO}) = -e(\phi_{red} + 4.40)\ (\text{eV}) \quad (2)$$

$$\mathbf{E}_{CV} = \phi_{red} + \phi_{red}\ (\text{eV}) \quad (3)$$

1.3. Synthesis

1-Bromo-4-(2-ethylhexyl)benzene (2). A solution of 2-ethylhexyl bromide (**1**) (60 mL, 0.336 mol) in 500 mL of diethyl ether was added dropwise to a suspension of magnesium (8.2 g, 0.341 mol) in 50 mL of diethyl ether. The mixture was refluxed for 1.5 hours and then was cooled down to the ambient temperature (a.t.). The resulting Grignard reagent was added dropwise to a solution of 1,4-dibromobenzene (65 g, 0.276 mol) and $Pd(dppf)Cl_2$ (580 mg, 1 mmol) in 100 mL of diethyl ether wile temperature was kept between 0 and 10 °C. The resulting mixture was allowed to rise to a.t. and stirring overnight. [Note: wile stirring, the reaction mixture can self-warm to a reflux]. After completion of the reaction, 500 mL of water was added to the reaction mixture followed by the addition 1M HCl (until acidic media). The organic phase was separated, washed with water and dried over sodium sulfate. The solvent was removed under reduced pressure. Excess of initial reagents was distilled off in a vacuum (1 mBar) and cube containing the product was passed over a short column of silica gel in hexane to give the compound **2** (63.6 g, 86%). Purity was estimated as 98% according to GC analysis.

^{1}H NMR (*J*, Hz, $CDCl_3$): δ (ppm) = 0.78-0.94 (m, 6H), 1.16-1.35 (m, 8H), 1.45-1.56 (m, 1H), 2.49 (d, *J*=7.02, 2H), 7.02 (m, *J*=8.55, 2H), 7.38 (m, *J*=8.24, 2H). ^{13}C NMR ($CDCl_3$): δ (ppm) = 10.7, 14.1, 23.0, 26.2, 28.8, 32.2, 39.5, 41.0, 119.2, 130.9, 131.1, 140.8. MALDI-MS: found m/z 268.19, calcd. 269.22.

4,4''-Bis(2-ethylhexyl)-1,1':4',1''- terphenyl (EH-3Ph-EH).

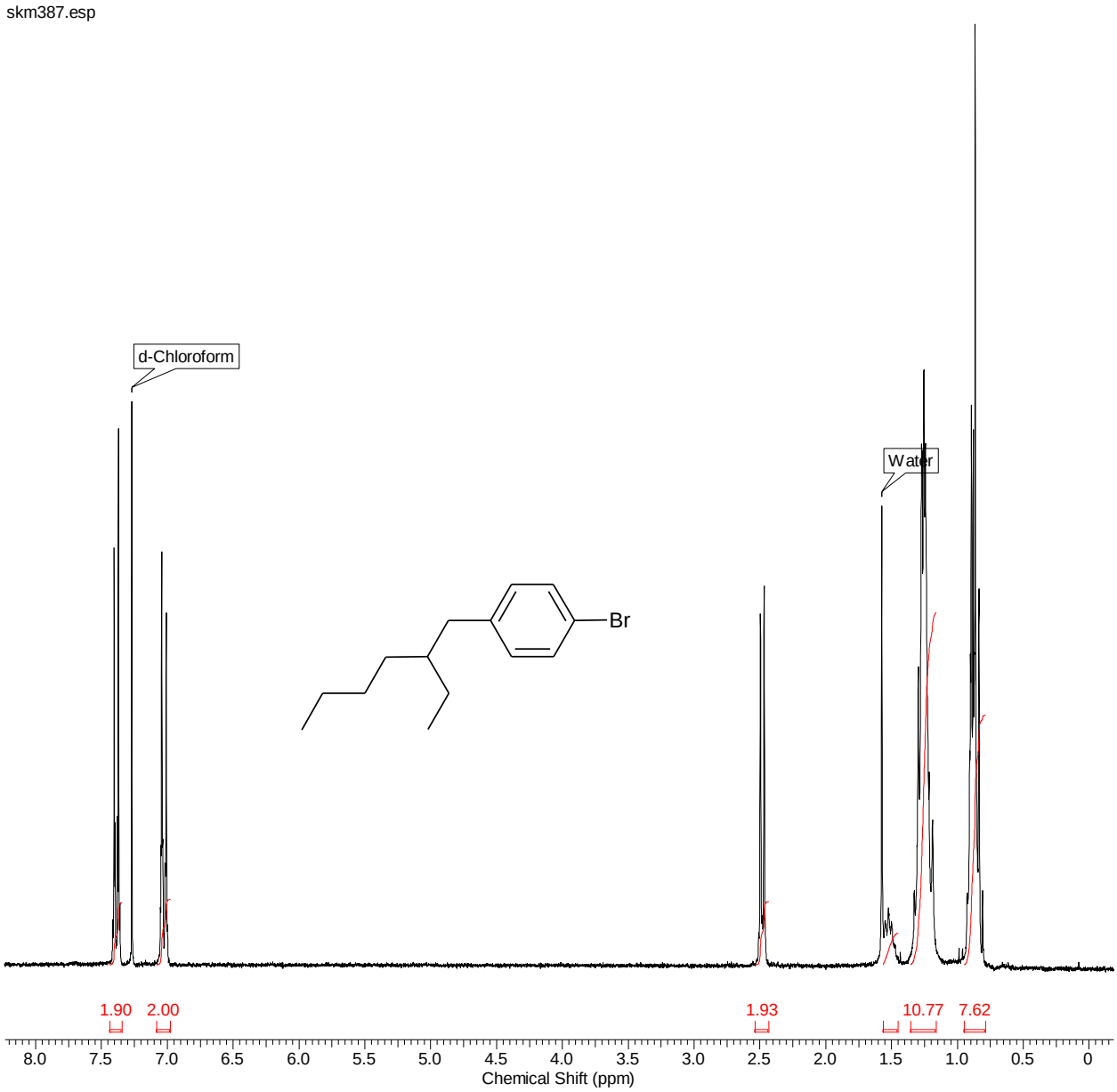
This compound was obtained by the method described above for **2** using compound **2** (20 g, 66.8 mmol), magnesium (1.68 g, 70 mmol), 1,4-dibromobenzene (7.49 g, 31.7 mmol) and Pd(dppf)Cl_2 (200 mg, 0.3 mmol). The crude product was passed over a short column of silica gel in toluene to remove the rest of the catalyst. The product was purified by recrystallization from hexane to give a 11.28 g of pure compound **EH-3Ph-EH** (78.5%).

^{1}H NMR (*J*, Hz, $CDCl_3$): δ (ppm) = 0.92 (t, J=7.32, 12H,), 1.23-1.42 (m, 16H), 1.55-1.69 (m, 2H), 2.59 (d, J=6.71, 4H), 7.20-7.27 (overlapping peaks, 4H), 7.57 (m, J=8.24, 4H), 7.68 (s, 4H). ^{13}C NMR ($CDCl_3$): δ (ppm) = 10.91, 14.29, 23.18, 25.50, 28.97, 32.44, 39.84, 41.18, 126.74, 127.31, 129.75, 138.02, 139.80, 141.18. Calc. for $C_{34}H_{46}$: C (89.80%); H (10.20). Found (%): C, 89.72; H, 10.27.

4,4”-Bis(trimethylsilyl)-1,1’ : 4‘,1”-terphenyl (TMS-3Ph-TMS). This compound was obtained by the method described elsewhere [4] using 1-bromo-4-(trimethylsilyl)benzene (**7**) (48 g, 0.21 mol), magnesium (5.31 g, 0.22 mol), 1,4-dibromobenzene (22 g, 93.2 mmol) and Pd(dppf)Cl_2 (340 mg, 0.46 mmol). The crude product was passed over a short column of silica gel in toluene to remove the rest of the catalyst. The product was purified by recrystallization from hexane to give a 30.45 g of pure compound **TMS-3Ph-TMS** (87%).

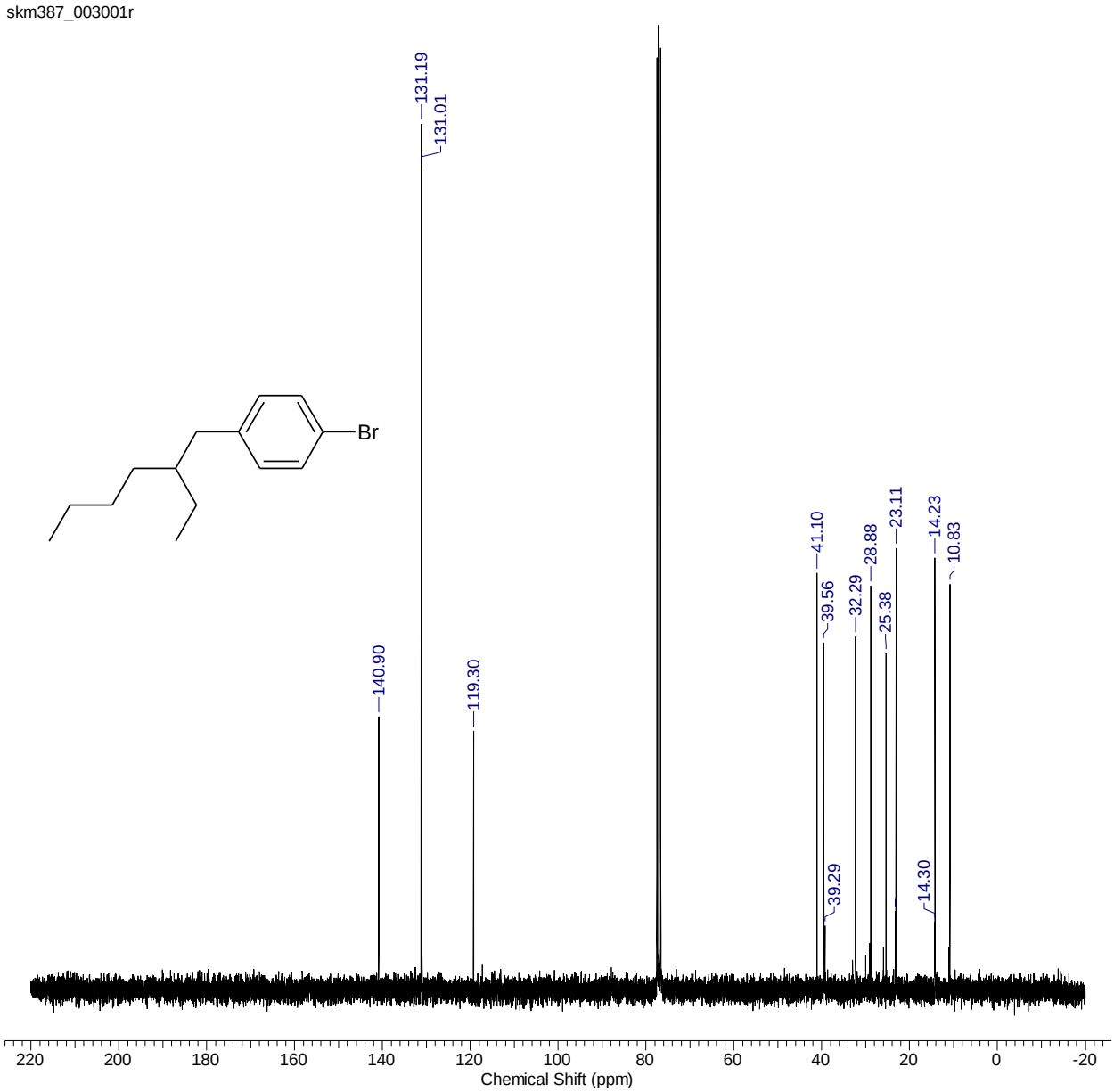
^{1}H NMR (*J*, Hz, $CDCl_3$): δ (ppm) = 0.33 (s, 18H), 7.65 (s, 8H), 7.70 (s, 4H). ^{13}C NMR ($CDCl_3$): δ (ppm) = -1.08, 126.36, 127.50, 133.87, 139.35, 140.12, 141.06. ^{29}Si NMR ($CDCl_3$): δ (ppm) = -3.95.

2. ^{1}H, ^{13}C, ^{29}Si NMR spectra



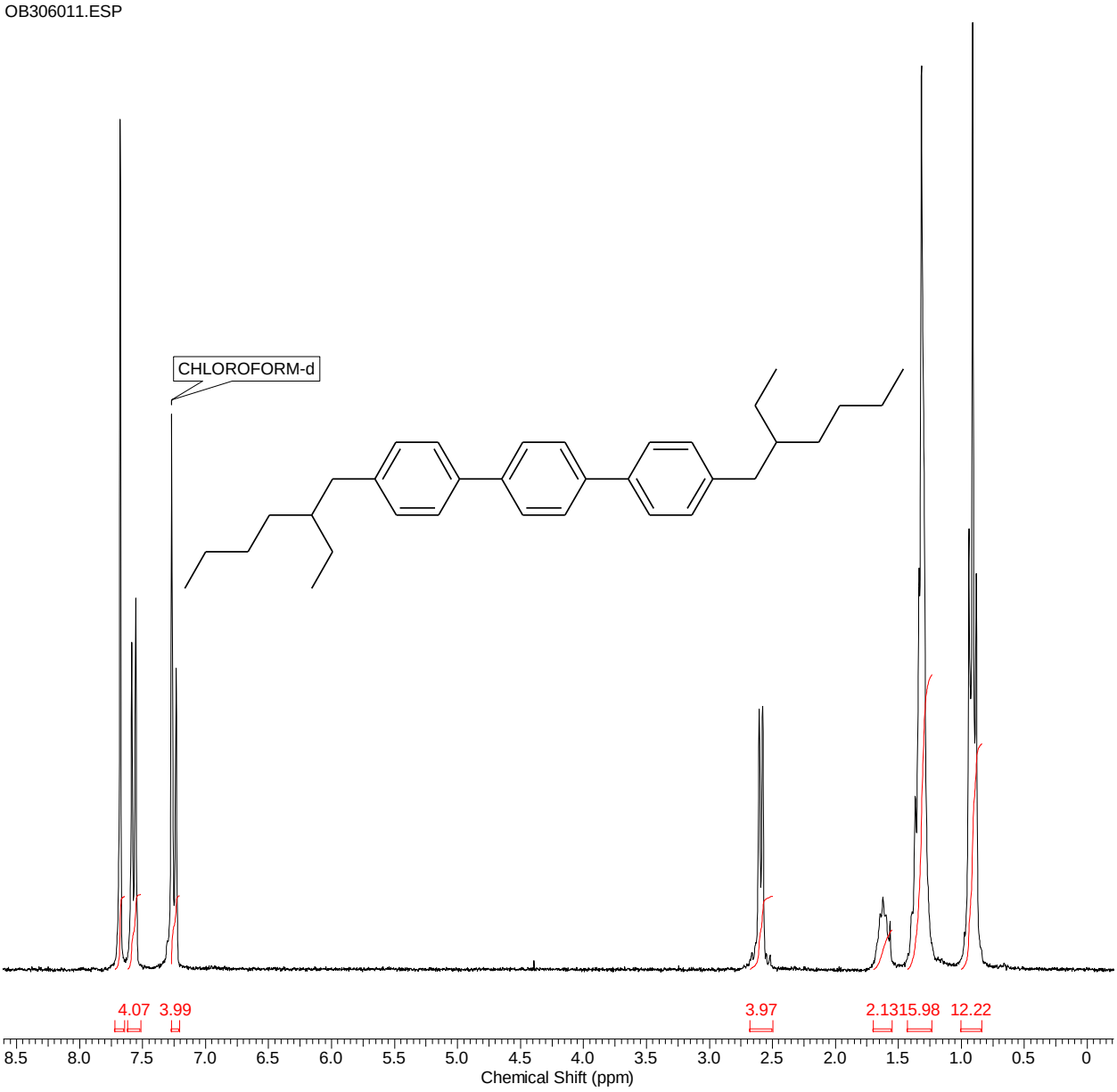
No.	(ppm)	Value	Absolute Value	Non-Negative Value
1	[0.7872 .. 0.9482]	7.62304783	7.26782400e+7	7.62304783
2	[1.1602 .. 1.3559]	10.77197170	1.02700120e+8	10.77197170
3	[1.4517 .. 1.5638]	0.97097671	9.25730500e+6	0.97097671
4	[2.4304 .. 2.5384]	1.93044794	1.84049160e+7	1.93044794
5	[6.9768 .. 7.0807]	2.00092793	1.90768740e+7	2.00092793
6	[7.3416 .. 7.4374]	1.90011311	1.81157040e+7	1.90011311

Figure S1. ^{1}H NMR spectrum of 1-bromo-4-(2-ethylhexyl)benzene (**2**).



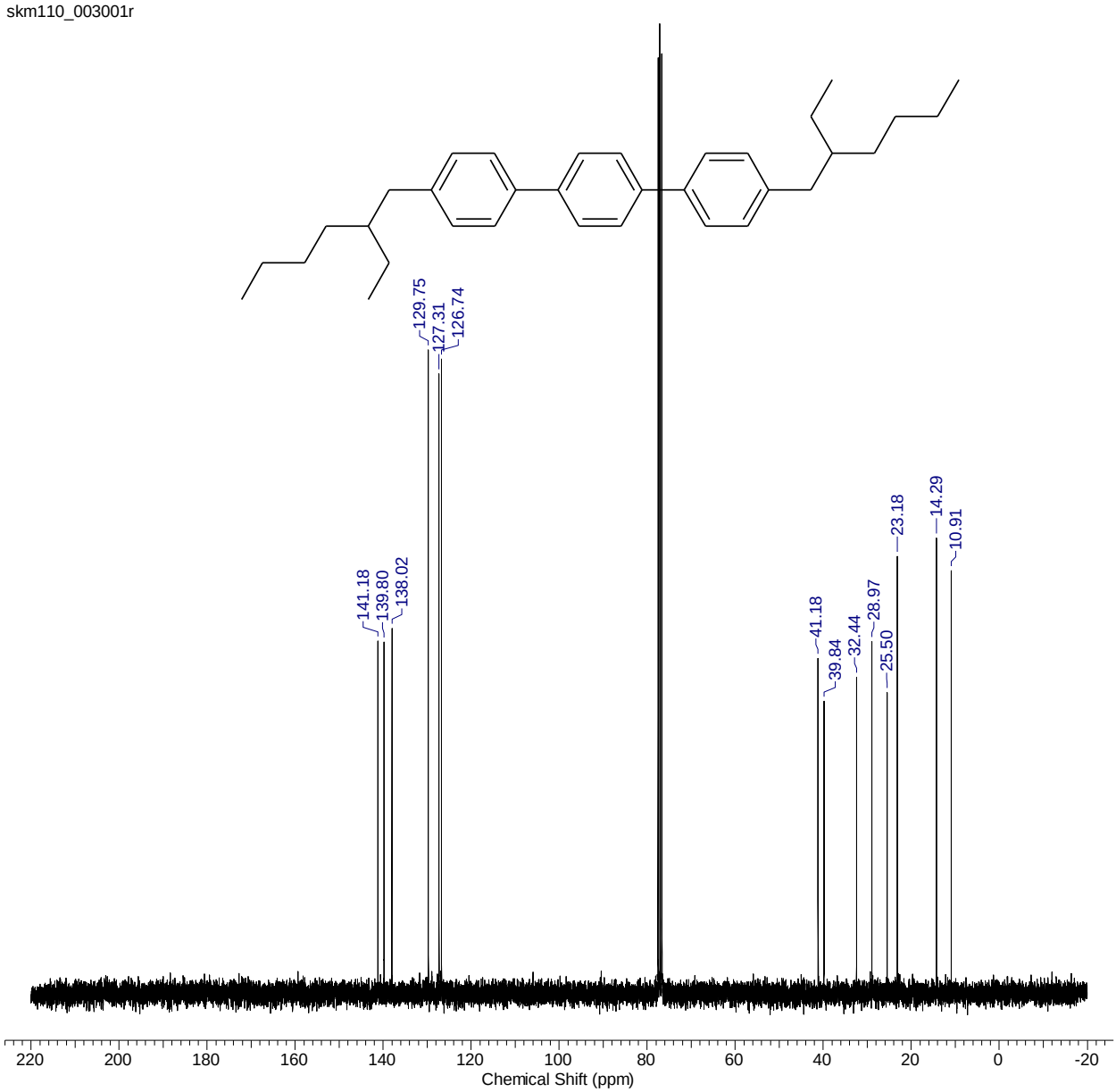
No.	(ppm)	Height
1	10.83	0.4202
2	14.23	0.4476
3	14.30	0.0699
4	23.11	0.4579
5	23.27	0.0808
6	25.38	0.3483
7	28.88	0.4188
8	32.29	0.3659
9	39.29	0.0661
10	39.56	0.3596
11	41.10	0.4317
12	119.30	0.2683
13	131.01	0.8539
14	131.19	0.8976
15	140.90	0.2832

Figure S2. ^{13}C NMR spectrum of 1-bromo-4-(2-ethylhexyl)benzene (**2**).



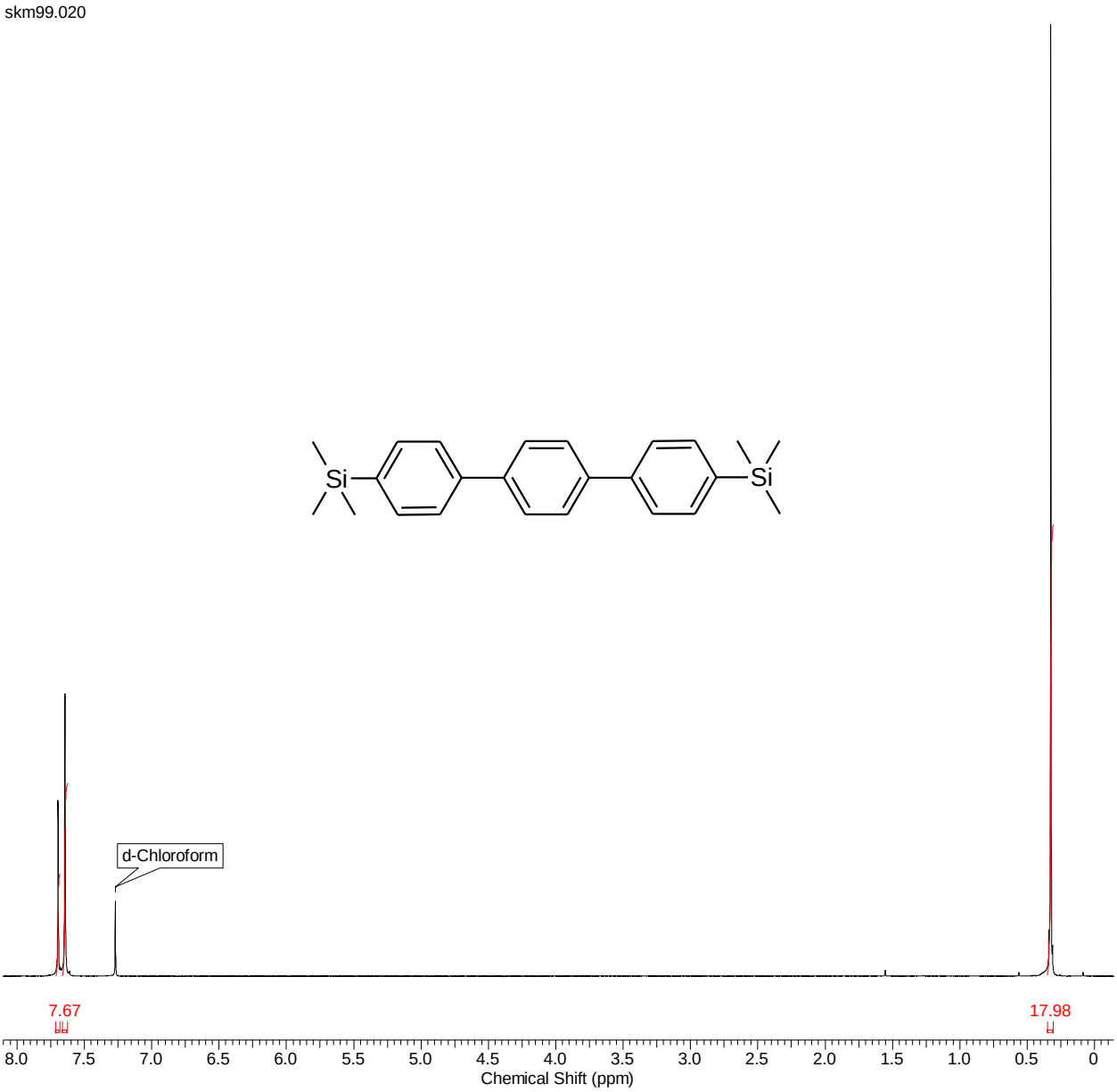
No.	(ppm)	Value	Absolute Value	Non-Negative Value
1	[0.8386 .. 1.0026]	12.22083378	4.94059080e+7	12.22083378
2	[1.2326 .. 1.4276]	15.98219872	6.46122040e+7	15.98219872
3	[1.5503 .. 1.6988]	2.12547350	8.59278100e+6	2.12547350
4	[2.4957 .. 2.6780]	3.96804786	1.60418680e+7	3.96804786
5	[7.2048 .. 7.2715]	3.99231935	1.61399920e+7	3.99231935
6	[7.5146 .. 7.6167]	4.06715631	1.64425390e+7	4.06715631
7	[7.6414 .. 7.7215]	3.96610546	1.60340150e+7	3.96610546

Figure S3. ^{1}H NMR spectrum of 4,4"-bis(2-ethylhexyl)-1,1':4',1"- terphenyl (**EH-3Ph-EH**).



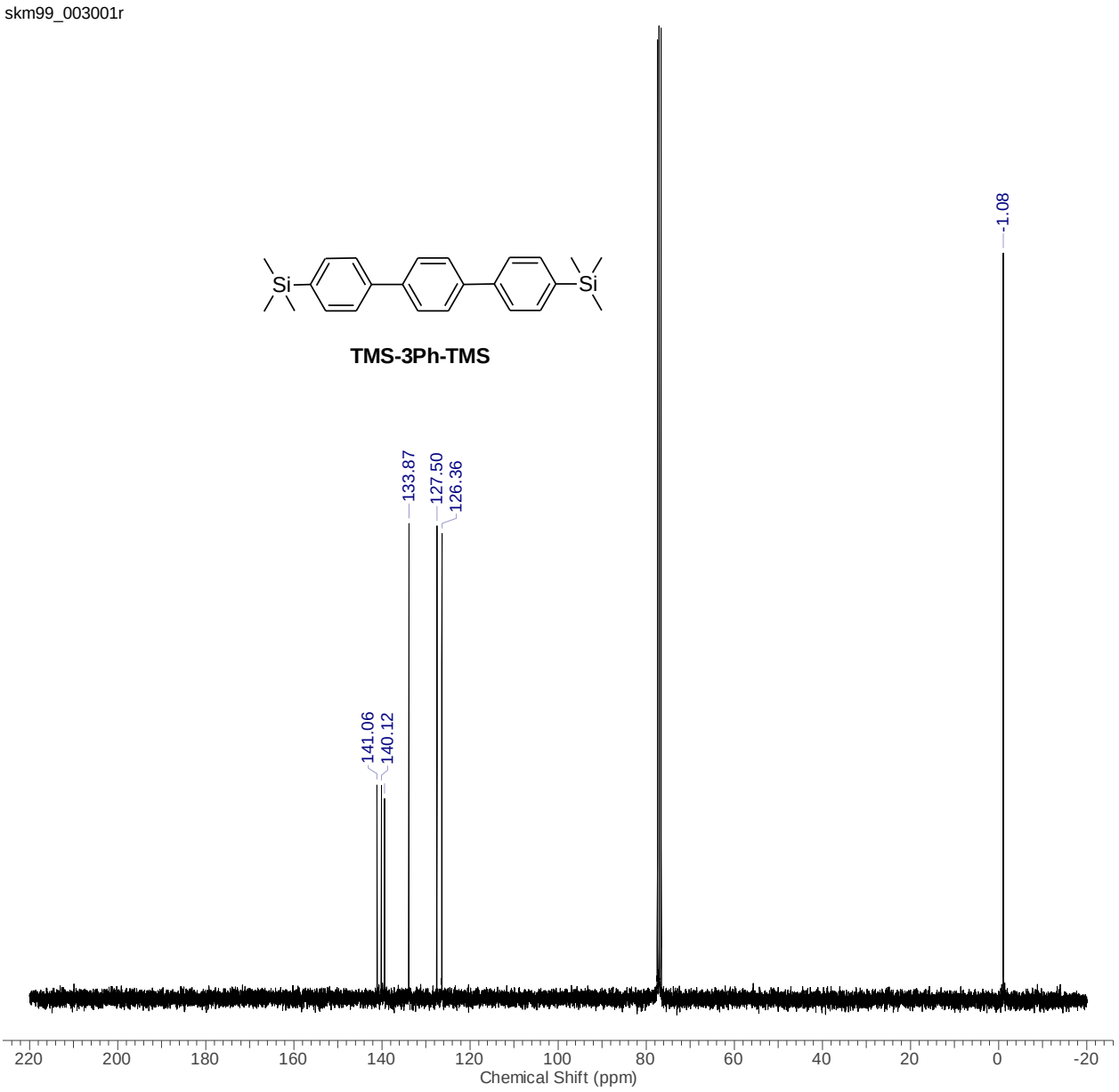
No.	(ppm)	Height
1	10.91	0.4357
2	14.29	0.4697
3	23.18	0.4505
4	25.50	0.3103
5	28.97	0.3626
6	32.44	0.3262
7	39.84	0.3012
8	41.18	0.3455
9	126.74	0.6541
10	127.31	0.6389
11	129.75	0.6634
12	138.02	0.3763
13	139.80	0.3622
14	141.18	0.3635

Figure S4. ^{13}C NMR spectrum of 4,4"-bis(2-ethylhexyl)-1,1':4',1"- terphenyl (**EH-3Ph-EH**).



No.	(ppm)	Value	Absolute Value	Non-Negative Value
1	[0.3059 .. 0.3493]	17.97665787	1.34042440e+7	17.97665787
2	[7.6232 .. 7.6617]	7.67483330	5.72271750e+6	7.67483330
3	[7.6811 .. 7.7100]	4.08661795	3.04717500e+6	4.08661795

Figure S5. ^{1}H NMR spectrum of 4,4”-bis(trimethylsilyl)-1,1’ : 4‘,1”-terphenyl (**TMS-3Ph-TMS**).



No.	(ppm)	Height
1	-1.08	0.7677
2	126.36	0.4820
3	127.50	0.4896
4	133.87	0.4924
5	139.35	0.2112
6	140.12	0.2249
7	141.06	0.2256

Figure S6. ^{13}C NMR spectrum of 4,4”-bis(trimethylsilyl)-1,1’ : 4‘,1”-terphenyl (**TMS-3Ph-TMS**).

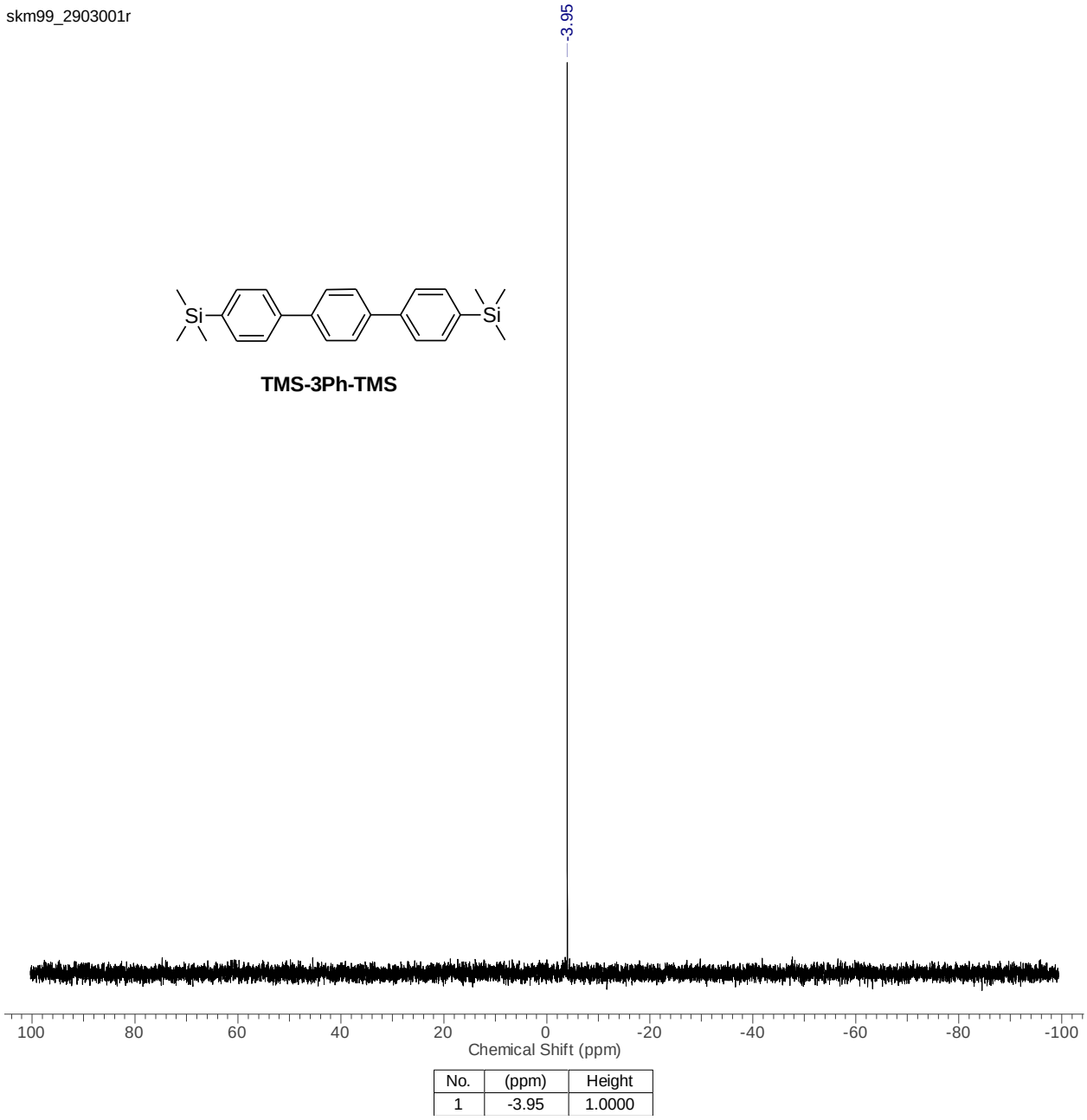
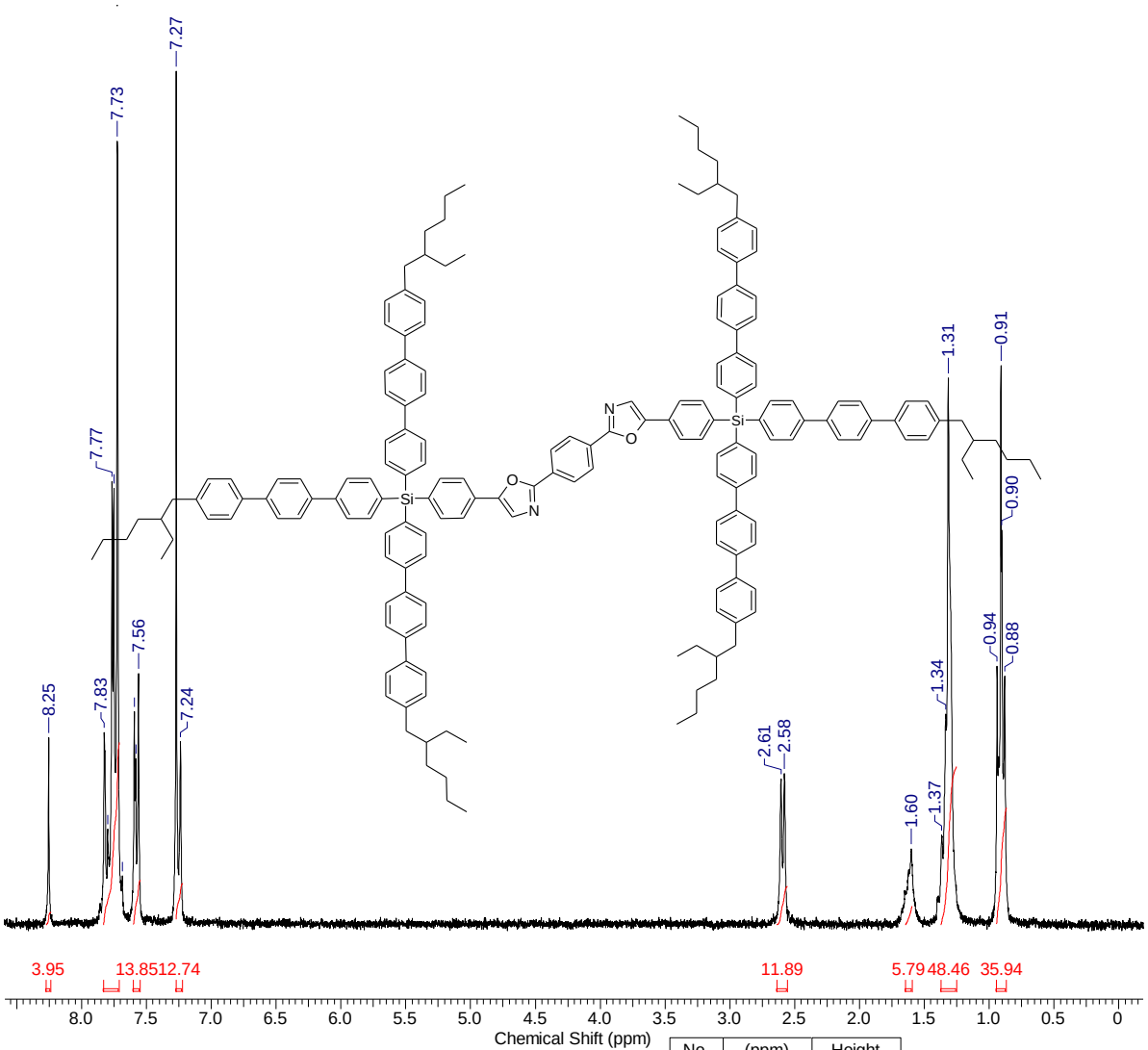


Figure S7. ^{29}Si NMR spectrum of 4,4”-bis(trimethylsilyl)-1,1’ : 4‘,1”-terphenyl (**TMS-3Ph-TMS**).

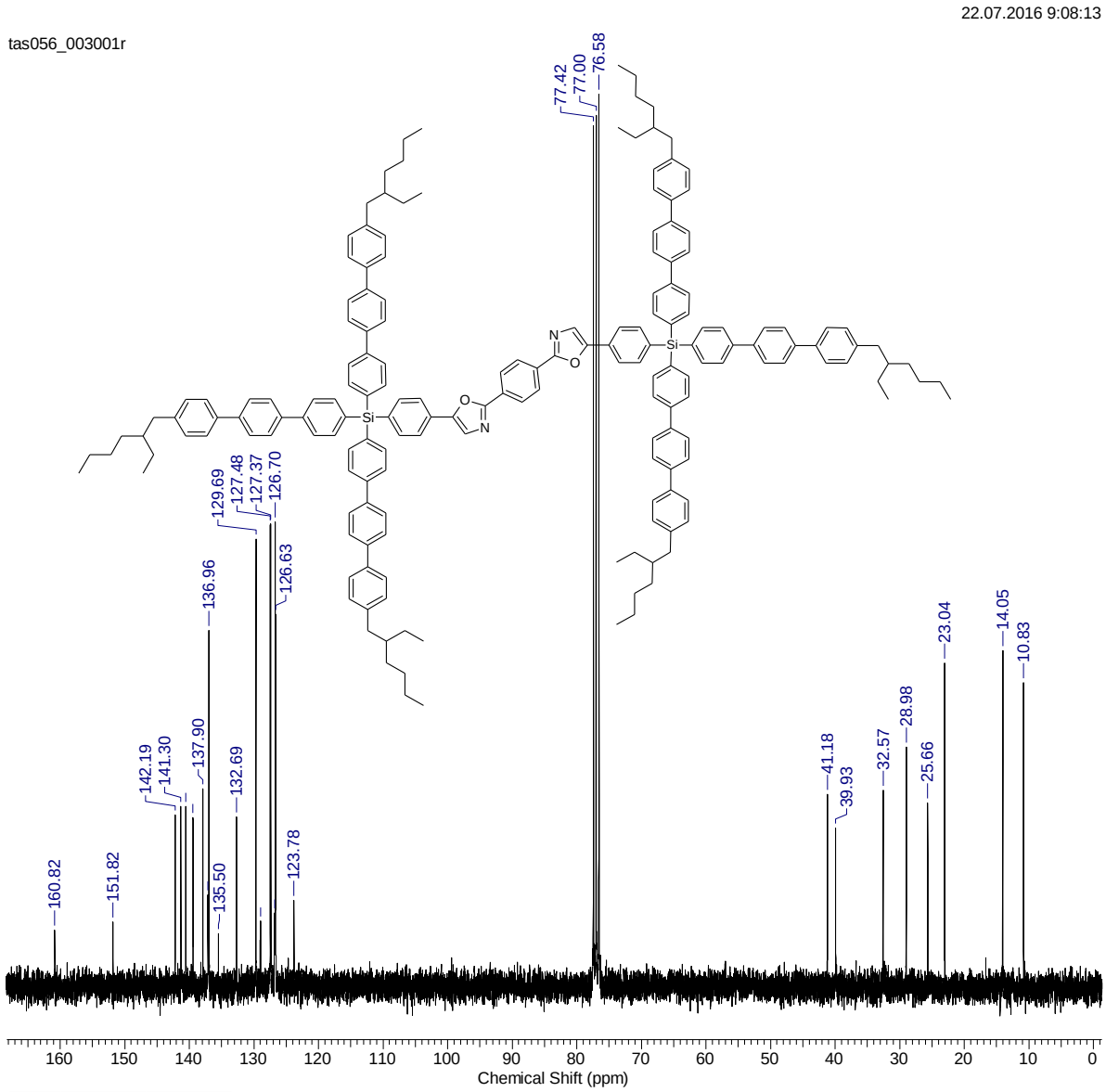
tas056.esp



No.	(ppm)	Value	Absolute Value	Non-Negative Value
1	[0.8654 .. 0.9424]	35.93564987	5.15101080e+7	35.93564987
2	[1.2515 .. 1.3701]	48.46119308	6.94642000e+7	48.46119308
3	[1.5939 .. 1.6450]	5.79270077	8.30324850e+6	5.79270077
4	[2.5545 .. 2.6377]	11.88838959	1.70408000e+7	11.88838959
5	[7.2209 .. 7.2698]	12.74423218	1.82675640e+7	12.74423218
6	[7.5472 .. 7.6003]	13.84723473	1.98486060e+7	13.84723473
7	[7.7083 .. 7.8305]	55.87973785	8.00979360e+7	55.87973785
8	[8.2383 .. 8.2760]	3.94903827	5.66054550e+6	3.94903827

No.	(ppm)	Height
1	0.88	0.2917
2	0.90	0.4625
3	0.91	0.6550
4	0.94	0.3030
5	1.31	0.6405
6	1.34	0.2471
7	1.37	0.1050
8	1.60	0.0892
9	2.58	0.1772
10	2.61	0.1711
11	7.24	0.2148
12	7.27	1.0000
13	7.56	0.2947
14	7.58	0.1950
15	7.59	0.2498
16	7.69	0.0575
17	7.73	0.9177
18	7.75	0.5117
19	7.77	0.5192
20	7.80	0.1127
21	7.83	0.2258
22	8.25	0.2196

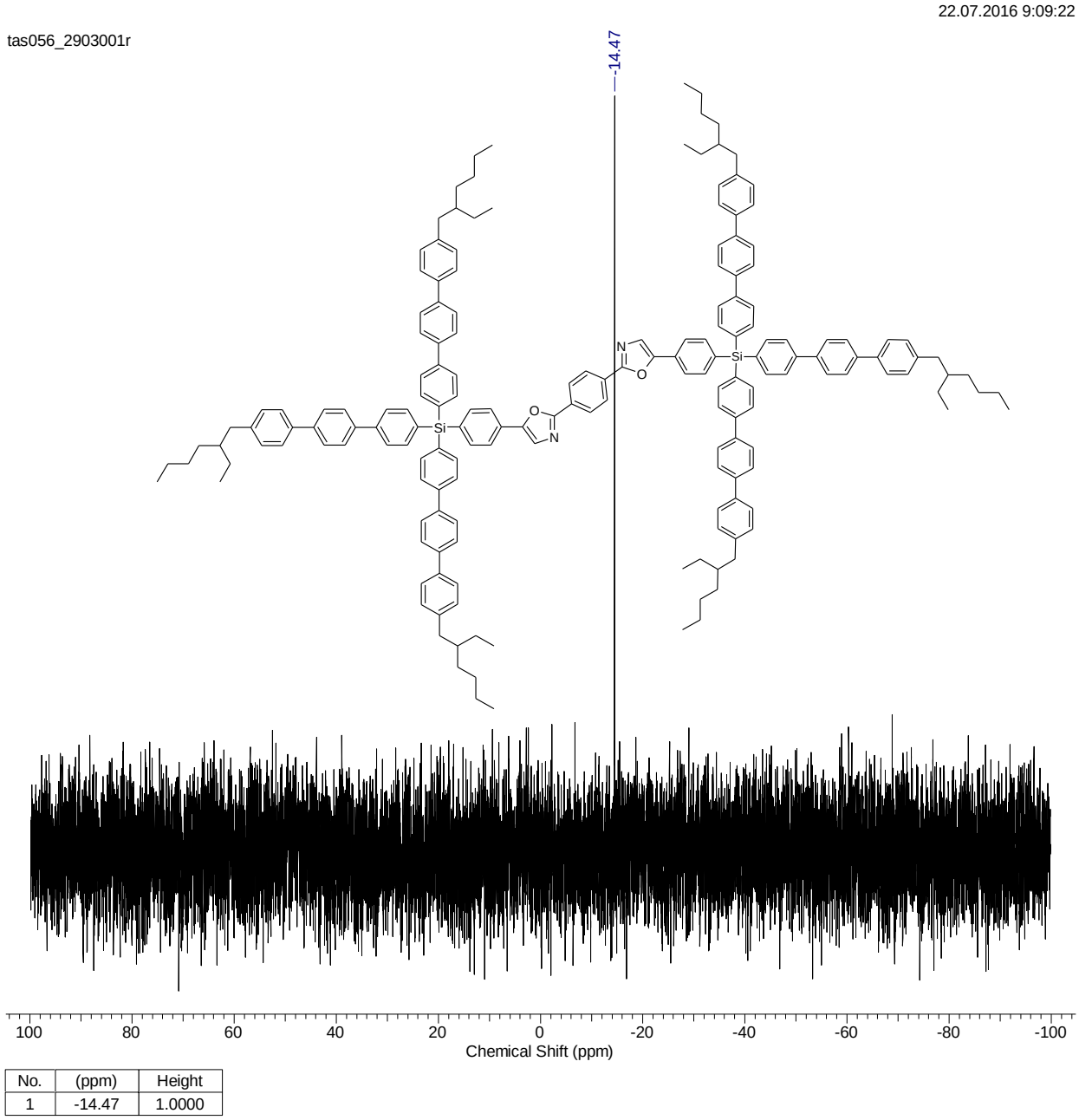
Figure S8. ^{1}H NMR spectrum of 2,2'-benzene-1,4-diylbis[5-(4-{tris[4''-(2-ethylhexyl)-1,1':4',1''-terphenyl-4-yl]silyl}phenyl)-1,3-oxazole] (**(POPOP)Si$_2$(3Ph-EH)$_6$**).



No.	(ppm)	Height
1	10.83	0.3506
2	14.05	0.3864
3	23.04	0.3724
4	25.66	0.2182
5	28.98	0.2798
6	32.57	0.2322
7	39.93	0.1909
8	41.18	0.2275
9	76.58	1.0000

No.	(ppm)	Height
10	77.00	0.9767
11	77.42	0.9652
12	123.78	0.1108
13	126.63	0.4262
14	126.70	0.5284
15	126.80	0.0971
16	127.37	0.5259
17	127.48	0.5247
18	128.95	0.0882
19	129.69	0.5095
20	132.69	0.2030
21	135.50	0.0742
22	136.96	0.4087
23	137.11	0.1167
24	137.90	0.2337
25	139.42	0.2022
26	140.54	0.2145
27	141.30	0.2145
28	142.19	0.2049
29	151.82	0.0867
30	160.82	0.0783

Figure S9. ^{13}C NMR spectrum of 2,2'-benzene-1,4-diylbis[5-(4-{tris[4"-(2-ethylhexyl)-1,1':4',1"-terphenyl-4-yl]silyl}phenyl)-1,3-oxazole] (**(POPOP)Si$_2$(3Ph-EH)$_6$**).



No.	(ppm)	Height
1	-14.47	1.0000

Figure S10. ^{29}Si NMR spectrum of 2,2'-benzene-1,4-diylbis[5-(4-{tris[4"-(2-ethylhexyl)-1,1':4',1"-terphenyl-4-yl]silyl}phenyl)-1,3-oxazole] (**(POPOP)Si$_2$(3Ph-EH)$_6$**).

3. Thermogravimetric analysis data

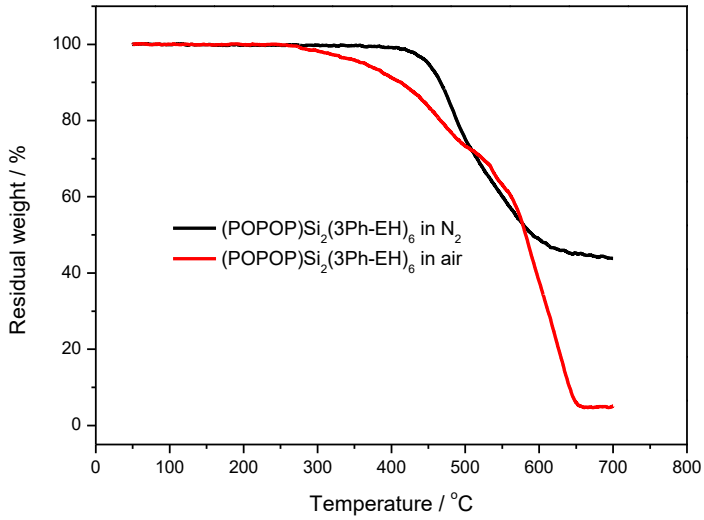


Figure S11. Thermogravimetric analysis (TGA) curves of **(POPOP)Si$_2$(3Ph-EH)$_6$**.

4. Differential scanning calorimetry data

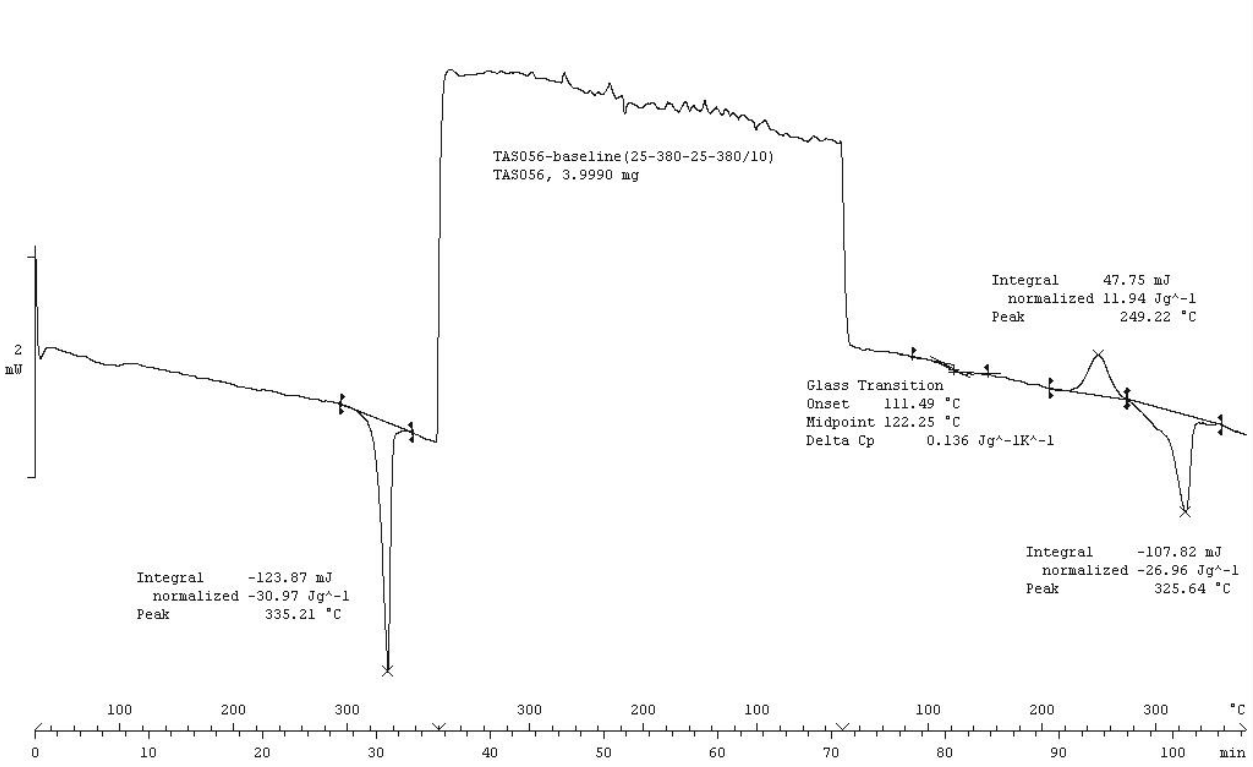


Figure S12. DSC curves of **(POPOP)Si$_2$(3Ph-EH)$_6$**.

5. Cyclic voltammetry curves

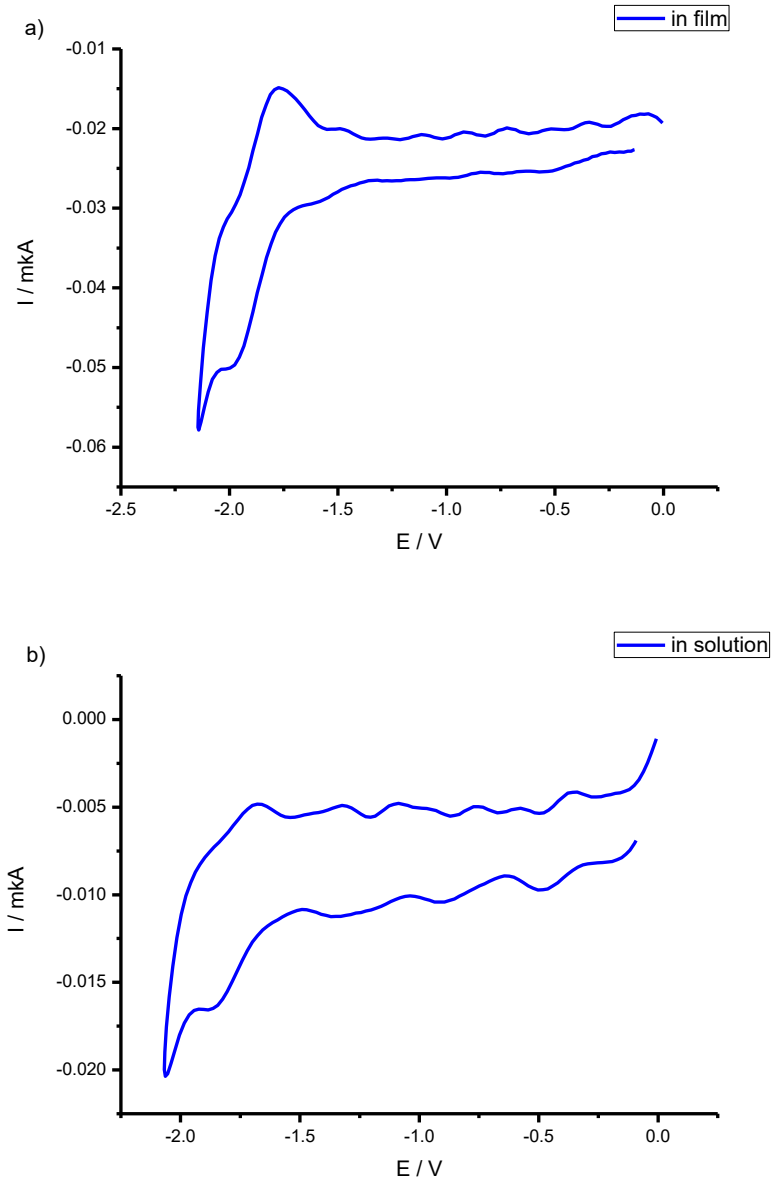


Figure S13. CV curves of **(POPOP)Si_2(3Ph-EH)$_6$** in thin film (a) and in diluted solution (b).

6. Static optical data

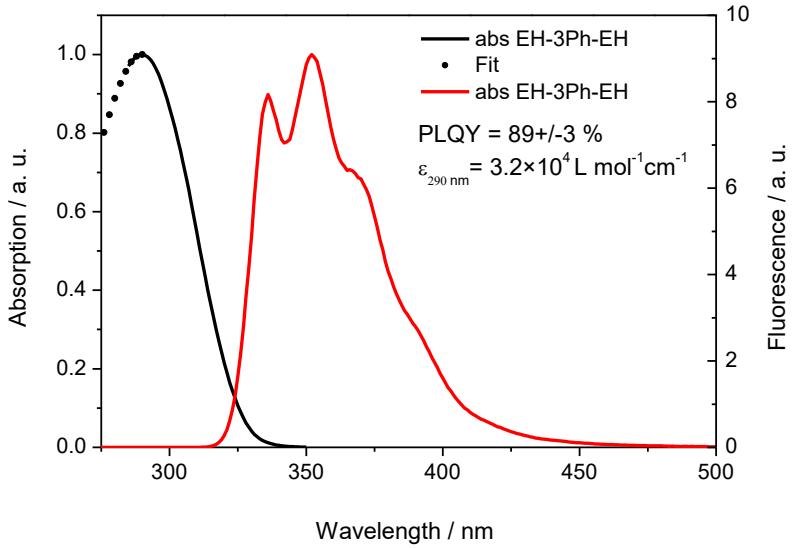


Figure S14. Absorption and fluorescence spectra of diluted solutions of **EH-3Ph-EH** in toluene.

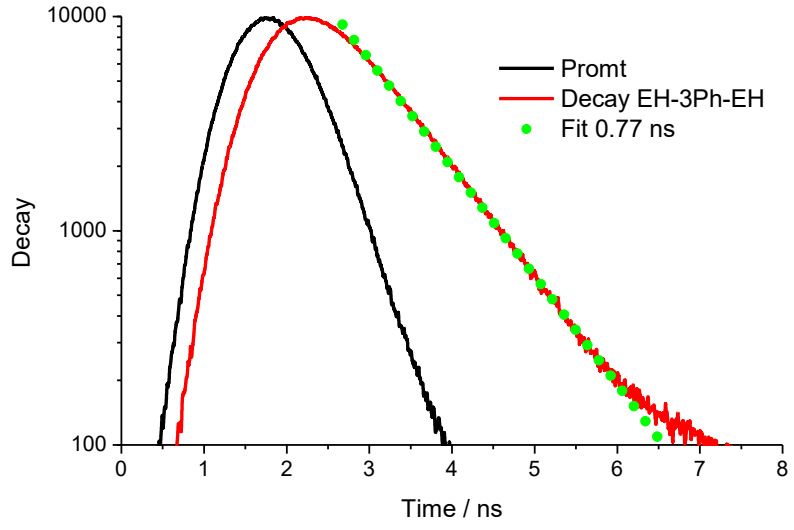


Figure S15. PL decay time measurements of diluted solutions **EH-3Ph-EH** in toluene.

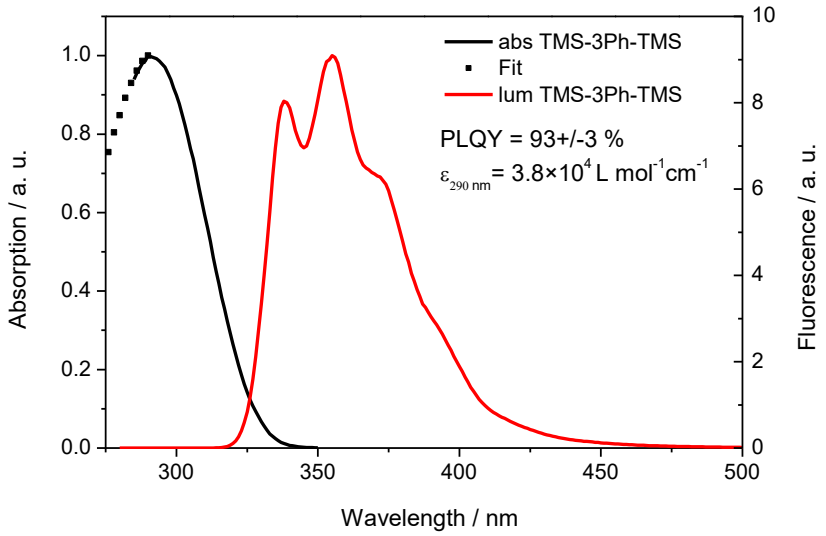


Figure S16. Absorption and fluorescence spectra of diluted solutions of **TMS-3Ph-TMS** in toluene.

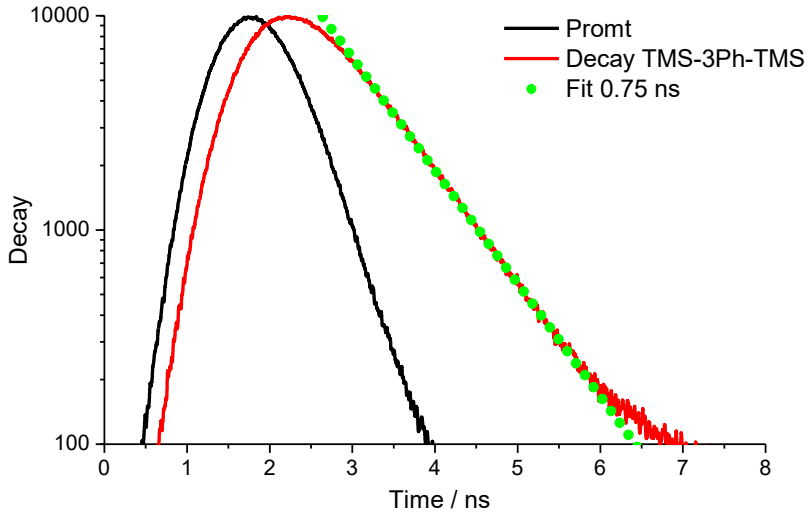


Figure S17. PL decay time measurements of diluted solutions of **TMS-3Ph-TMS** in toluene.

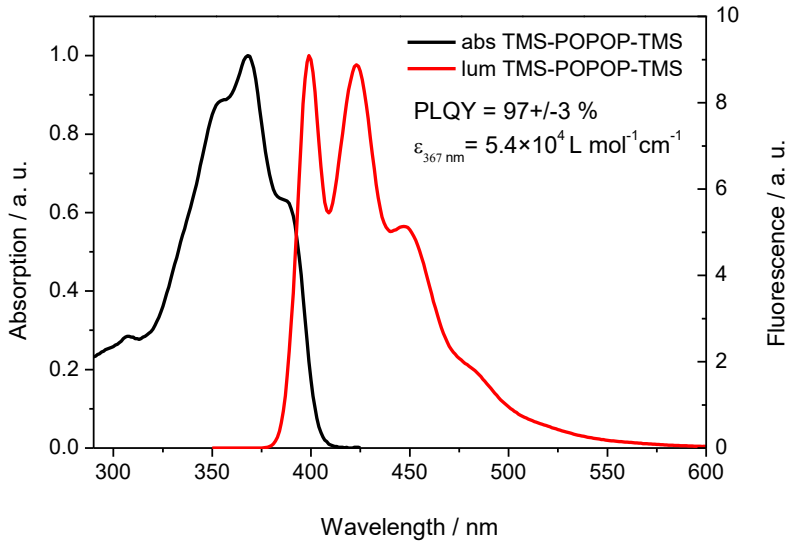


Figure S18. Absorption and fluorescence spectra of diluted solutions of **TMS-POPOP-TMS** in toluene.

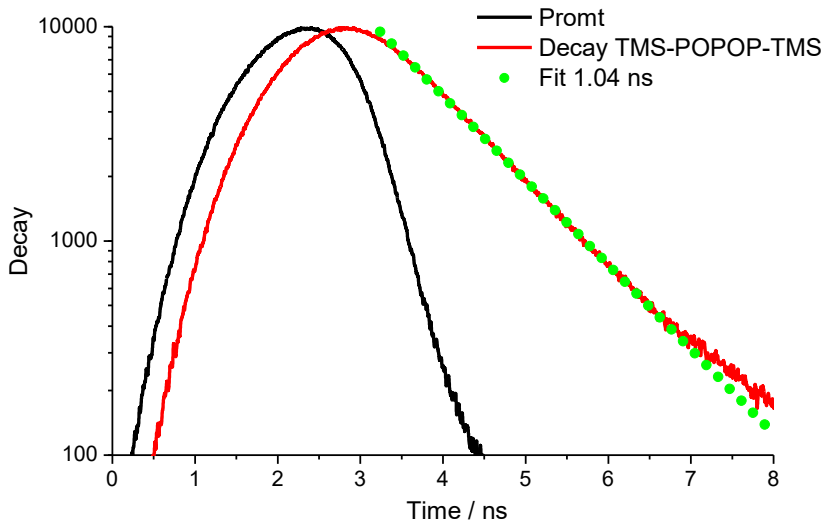


Figure S19. PL decay time measurements of diluted solutions of **TMS-POPOP-TMS** in toluene.

7. DFT calculations data

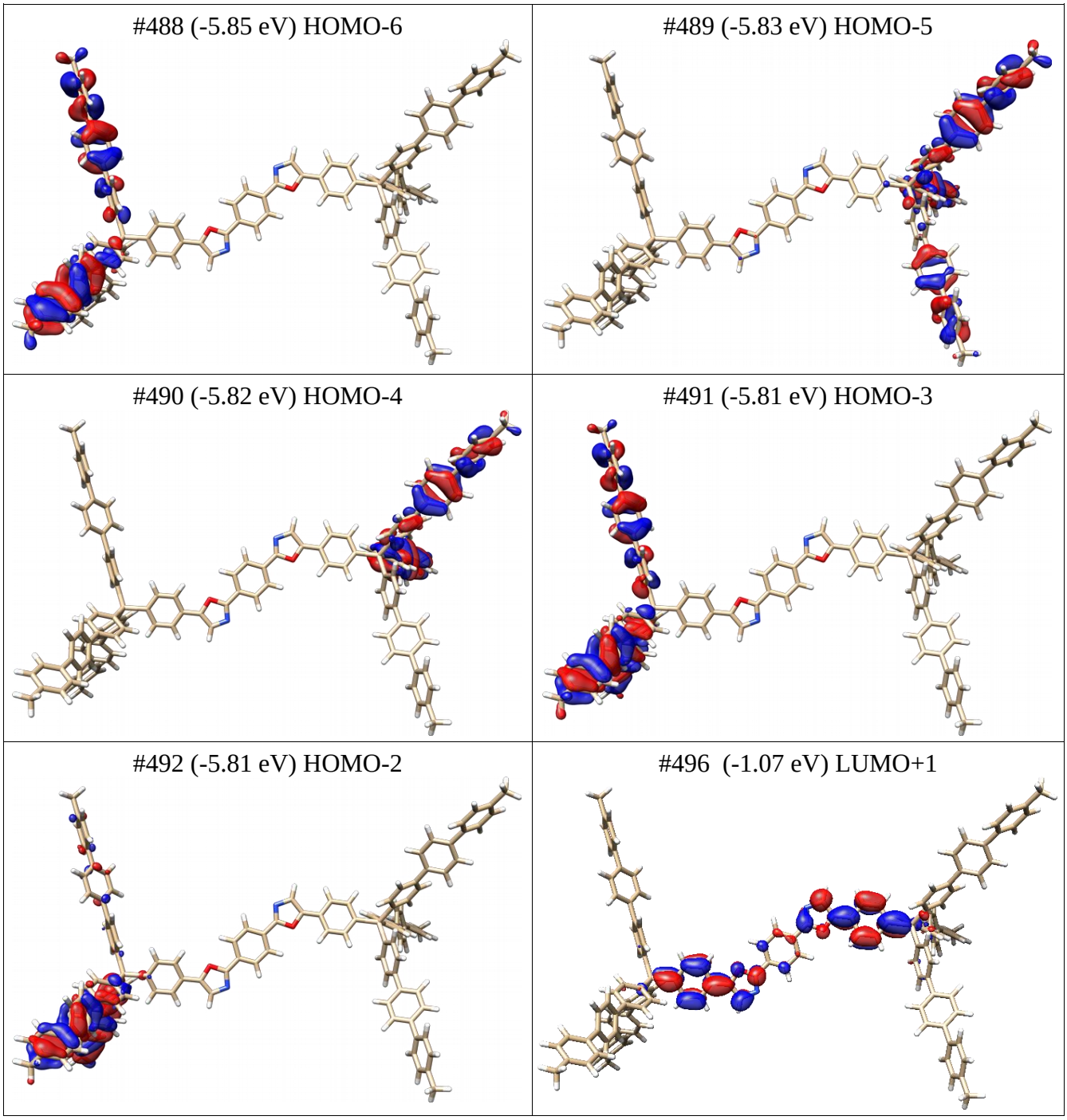


Figure S20. Isosurface (±0.025) contour diagrams of the molecular orbitals of **(POPOP)Si_2(3Ph-EH)$_6$**.

8. Transient absorption data

8.1. Transient absorption maps of p-terphenyl and POPOP in chloroform

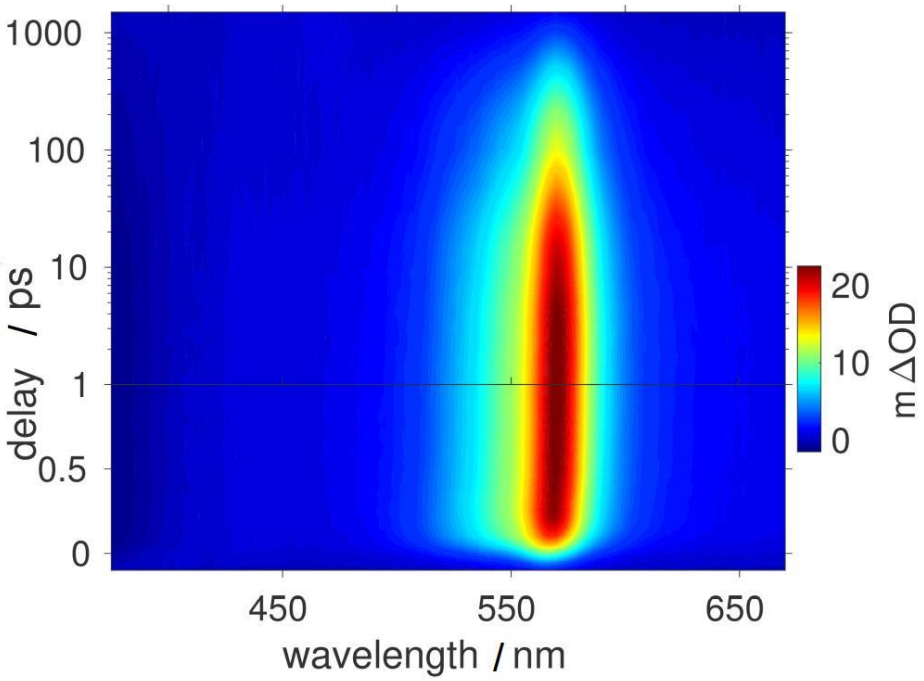


Figure S21. Transient absorption map of **3Ph** in chloroform.

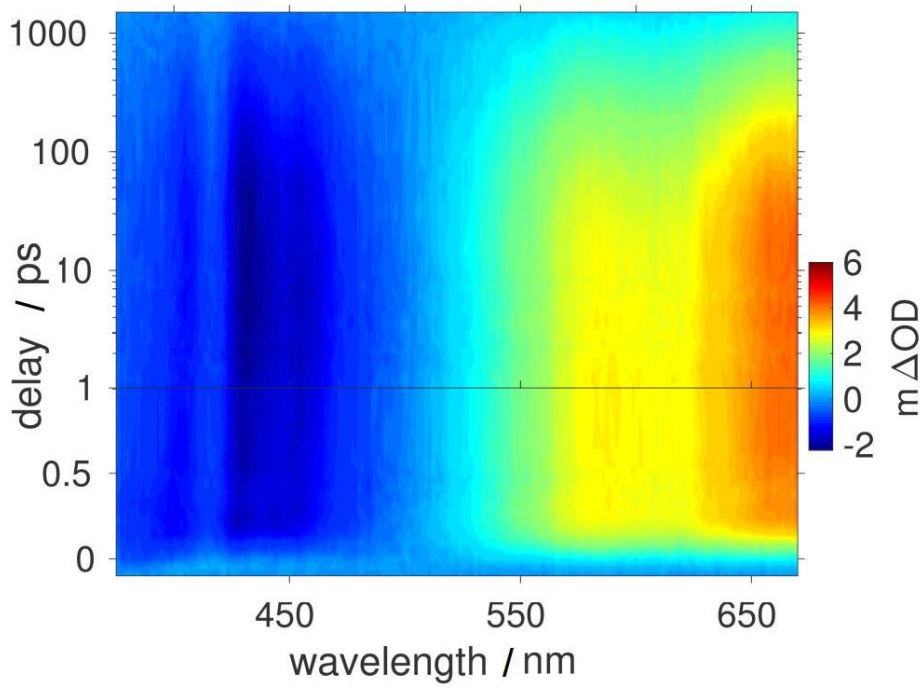


Figure S22. Transient absorption map of **POPOP** in chloroform.

8.2 Table of obtained fitting parameters

Table S1. Fitting parameters obtained from global analysis with models shown in Fig. 8.

Compound	k_1 (ps^{-1})	dk_1 (ps^{-1})	k_2 (ps^{-1})	dk_2 (ps^{-1})	k_3 (ps^{-1})	dk_3 (ps^{-1})	τ_1 (ps)	$d\tau_1$ (ps)	τ_2 (ps)	$d\tau_2$ (ps)	τ_3 (ps)	$d\tau_3$ (ps)
EH-3Ph-EH	2.39	0.019	0.0021	5.6×10^{-6}	--	--	**0.418**	0.0034	**473**	1.3	--	--
TMS-3Ph-TMS	2.60	0.015	0.0012	8.5×10^{-6}	--	--	**0.385**	0.0022	**804**	5.9	--	--
TMS-POPOP-TMS	12.2	0.064	0.78	0.011	0.00101	5.6×10^{-6}	**0.082**	0.0004	**1.27**	0.02	**991**	5.6
(POPOP)- Si_2(3Ph-EH)$_6$	9.6	0.043	0.79	0.014	0.00111	7.4×10^{-6}	**0.104**	0.0005	**1.26**	0.02	**901**	6.0

8.3 Calculation of the radiative and ISC lifetimes

Table S2. Calculation of the radiative and ISC lifetimes.

Compound	τ_{dec} (ps)	k_{dec} (ps^{-1})	PLQY	k_{rad} (ps^{-1})	k_{ISC} (ps^{-1})	τ_{ISC} (ns)	τ_{rad} (ps)
EH-3Ph-EH	473	0.0021	0.89	0.00188	0.000233	**4.3**	**531**
TMS-3Ph-TMS	804	0.0013	0.93	0.00117	0.000088	**11.4**	**864**
TMS-POPOP-TMS	991	0.0010	0.97	0.00098	0.000030	**33**	**1022**
(POPOP)Si_2(3Ph-EH)$_6$	901	0.00112	0.94	0.00105	0.000067	**15**	**953**

Notes: τ_{dec} – time constant of the decay of the measured transient absorption (TA) of the S_1 states, $k_{dec} = 1/\tau_{dec}$ – S_1 decay rate, PLQY = k_{rad}/k_{dec} – photoluminesce quantum yield, k_{rad} – radiative rate of the observed TA decay, k_{ISC} – intersystem crossing rate with $k_{dec} = k_{rad} + k_{ISC}$, $\tau_{ISC} = 1/k_{ISC}$ – intersystem crossing lifetime, $\tau_{rad} = 1/k_{rad}$ – radiative lifetime.

8.4. Fits of kinetic traces extracted from the target analysis modelling

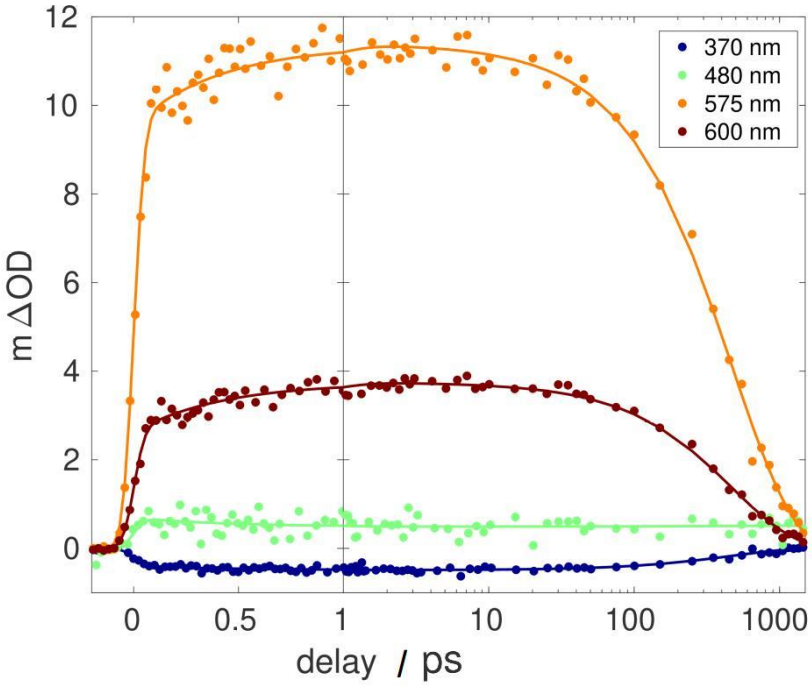


Figure S23. Experimental (symbols) and fitted (lines) kinetics traces for **EH-3Ph-EH**.

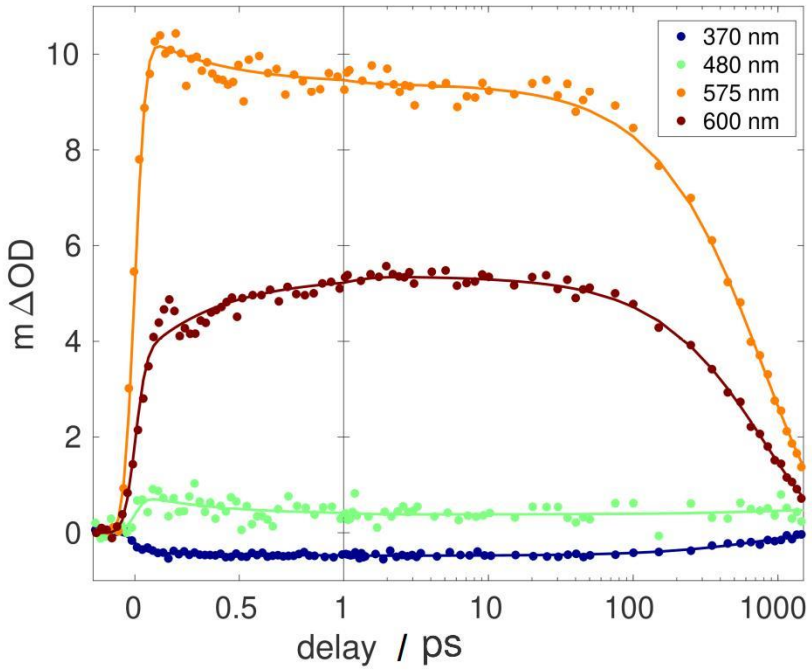


Figure S24. Experimental (symbols) and fitted (lines) kinetics traces for **TMS-3Ph-TMS**.

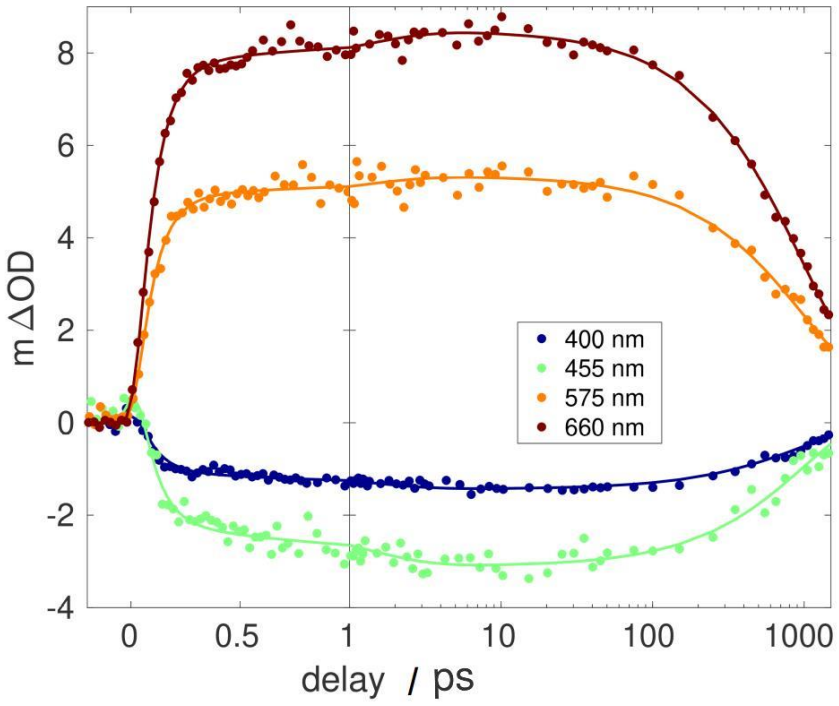


Figure S15. Experimental (symbols) and fitted (lines) kinetics traces for **TMS-POPOP-TMS**.

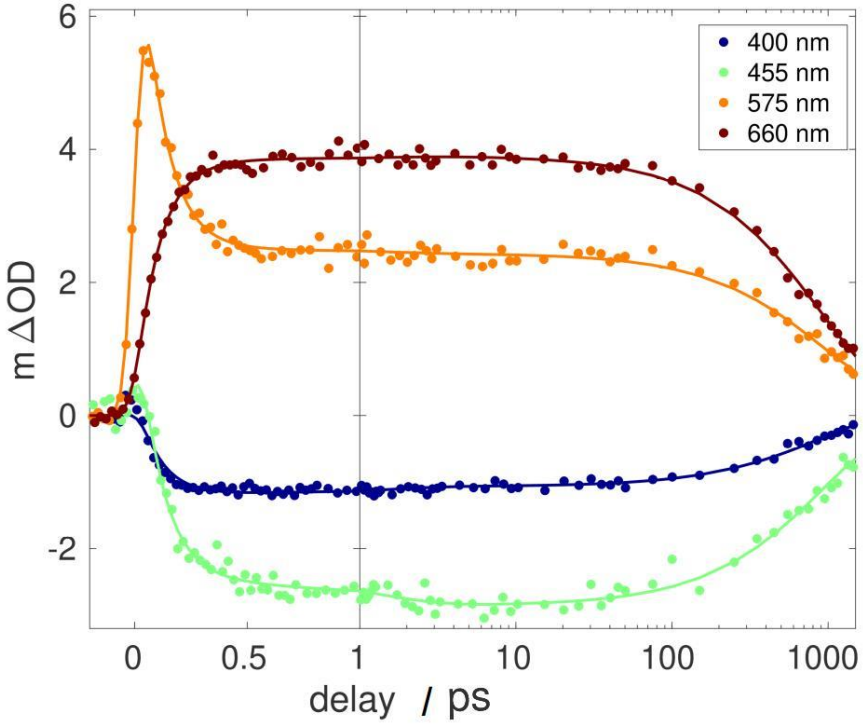


Figure S26. Experimental (symbols) and fitted (lines) kinetics traces for the **NOL**.

References

1. Skorotetcky, M.S.; Borshchev, O.V.; Surin, N.M.; Odarchenko, Y;. Pisarev, S.A.; Peregudova, S.M.; Törnroos, K.W.; Chernyshov, D.; Ivanov, D.A.; Ponomarenko, S.A. Synthesis and photostability of 1,4-bis(5-phenyloxazol-2-yl)benzene(POPOP) structural isomers and their trimethylsilyl derivatives, *Dyes and Pigments* **2017**, 141, 128–136. https://doi.org/10.1016/j.dyepig.2017.02.006
2. Ponomarenko, S. A.; Rasulova, N. N.; Luponosov, Y. N.; Surin, N. M.; Buzin, M. I.; Leshchiner, I.; Peregudova, S. M.; Muzafarov, A. M. Bithiophenesilane-Based Dendronized Polymers: Facile Synthesis and Properties of Novel Highly Branched Organosilicon Macromolecular Structures. *Macromolecules* **2012**, *45* (4), 2014–2024. https://doi.org/10.1021/ma2024045
3. Ponomarenko, S. A.; Kirchmeyer, S.; Elschner, A.; Alpatova, N. M.; Halik, M.; Klauk, H.; Zschieschang, U.; Schmid, G. Decyl-End-Capped Thiophene−Phenylene Oligomers as Organic Semiconducting Materials with Improved Oxidation Stability. *Chem. Mater.* **2006**, *18* (2), 579–586. https://doi.org/10.1021/cm052210m
4. Postnikov, V. A.; Sorokina, N. I.; Alekseeva, O. A.; Kulishov, A. A.; Sokolnikov, R. I.; Lyasnikova, M. S.; Grebenev, V. V.; Borshchev, O. V.; Skorotecky, M. S.; Surin, N. M.; et al. Growth from Solutions, Structure, and Photoluminescence of Single-Crystal Plates of p-Terphenyl and Its Trimethylsilyl Derivative. *Crystallogr. Reports* **2018**, *63* (5), 819–831. https://doi.org/10.1134/S1063774518050243