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Novel organic luminophores with benzene-1,3,5-triyl branching units

Lev L. Levkov, Oleg V. Borshchev, Sergey A. Pisarev, Yury V. Fedorov,
Evgeniya A. Svidchenko, Nikolay M. Surin and Sergey A. Ponomarenko

Contents:

1. General information

1.1 Starting materials

Synthesis of 1,5-dibromo-3-trimenthylsilylbenzene,[S1] 2-[4-(2-ethylhexyl)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[S2], 2-[4'-(2-ethylhexyl)biphenyl-4-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[S3] and 4,7-dibromo-2,1,3-benzothiadiazole[S4] was conducted by referred techniques. Commercially available $Pd(PPh_3)_4$, Na_2CO_3, pinacol и BBr_3 were used as received.

1.2 Methods and instrumentation

Solvent preparation was carried out using standard methods. Synthesis of all compounds was carried out in an argon atmosphere. The progress of the reactions and the purity of the products were monitored by GPC on a Shimadzu instrument (Japan) with an SPD-M10AV^{vp} diode matrix used as a detector, a Phenomenex column (USA), 7.8×300 mm with Phenogel sorbent (pore diameter 500 Å), THF eluent, column temperature 40°C and flow rate 1 ml/min. For purification by column chromatography, silica gel 60Å “Merck” (Germany) was used. Fractionation control was carried out by thin layer chromatography using Sorbfil plates (Russia). ^{1}H NMR spectra were recorded on a Bruker WP250 SY spectrometer (250.13 MHz), using the residual $CDCl_3$ signal (δ 7.27 ppm) as an internal standard. ^{13}C NMR spectra were recorded on a Bruker Advance II 300 spectrometer at an operating frequency of 75 MHz. In the case of ^{1}H NMR spectroscopy, the analyzed compounds were taken in the form of 0.5% solutions in $CDCl_3$. In the case of ^{13}C NMR spectroscopy, the analyzed compounds were taken in the form of 1–3% solutions in $CDCl_3$. The spectra were then processed on a computer using ACD Labs software. High-resolution mass spectra (HRMS) were recorded on a Bruker micrOTOF II instrument using electrospray ionization (ESI). The measurements were performed in a positive ion mode (interface capillary voltage – 4500 V); mass range from m/z 50 to m/z 3000 Da; external calibration with Electrospray Calibrant Solution.

Thermogravimetric analysis was carried out in dynamic mode in the range of 30–800°C using a Mettler Toledo TG50 system equipped with an M3 microbalance, which allows measuring the mass of samples in the range of 1–150 mg with an accuracy of 1 μg. The heating rate was chosen to be 20°C/min. DSC curves were obtained using a Mettler Toledo DSC30 system at a heating rate of 20 °C/min.

Spectrally pure solvent THF was used in optical studies. Absorption spectra of molecular solutions of compounds in THF were measured on a UV-2501PC spectrophotometer Shimadzu. To reduce the error in determining the extinction coefficient, measurements were performed at two concentrations: 10^{-5} mol/L and 2×10^{-6} mol/L. Luminescence spectra of molecular solutions of the studied compounds were measured on a spectrophotometer-spectrofluorometer

FLUORAN-2 VNIIOFI. Quantum yield was determined by the method of measuring the fluorescence of optically diluted solutions ($\varepsilon Cl<0.1$)[S5] using POPOP as the standard.[S6] The fluorescence lifetime was measured with the correlated photon counting mode on a Horiba Jobin Yvon Fluorolog 3-221 spectrofluorometer, LED 369 nm.

Quantum-chemical DFT-calculations were conducted in approximation PBE0 using basis set 6-31G[dp] in ORCA5 program. [S7]

2. **Synthetic procedures**

2.1. *Synthesis of [4,4''-bis(2-ethylhexyl)[1,1':3',1''-terphenyl]-5'-yl]trimethylsilane (**5**)*

A mixture of (3,5-dibromophenyl)trimethylsilane (1.33 g, 4.0 mmol), boronic acid ester **3** (3.25 g, 10 mmol), $Pd(PPh_3)_4$ (0.10 g, 0.09 mmol), toluene (50 ml), Na_2CO_3 (5 ml, 2M aq.)and ethanol (5 ml) was boiled with stirring for 19 hours. Extraction of the product from the reaction mixture was carried out with toluene. Purification was carried out by column chromatography on silica gel. Eluent – cyclohexane. After purification, 1.68 g of product was obtained containing no more than 10% impurities (GPC) (yield 80% relative to (3,5-dibromophenyl)trimethylsilane). NMR-^{1}H, δ, ppm: 0.35 (s, 9 H) 0.91 (t, *J*=7.32 Hz, 12 H) 1.19 - 1.47 (m, 18 H) 2.60 (d, *J*=6.41 Hz, 4 H), 7.21-7.30 (m, 4 H (overlapped with $CHCl_3$) 7.57 (d, *J*=7.94 Hz, 4 H) 7.69 (m,2 H) 7.77 (t, *J*=3.66 Hz 1 H). NMR-^{13}C, δ, ppm:-1.00, 10.78, 14.18, 23.07, 25.35, 28.84, 32.30, 39.71, 41.06, 126.59, 127.02, 129.58, 130.70, 138.78, 140.94, 141.05, 141.34. ESI-MS (TOF) m/z: [M+H]+ calculated for $C_{37}H_{54}SiH^+$ 527.4068, found: m/z [M+H]+ 527.4050.

2.2. *Synthesis of [4,4""-bis(2-ethylhexyl)[1,1’:4’,1”:3”,1”’:4”’,1””-quinquephenyl]-5”-yl]-trimethylsilane (**6**)*

A mixture of (3,5-dibromophenyl)trimethylsilane (1.22 g), boronic acid ester **4** (3.41 g, 9.0 mmol), $Pd(PPh_3)_4$ (0.25 g, 0.2 mmol), toluene (50 ml), Na_2CO_3 (5 ml, 2M aq.)and ethanol (5 ml) were boiled with stirring for 24 hours. Extraction of the product from the reaction mixture was carried out with toluene. Purification was carried out using silica gel column chromatography. Eluent – cyclohexane. After purification, 1.51 g of product was obtained containing no more than 5% impurities (GPC) (yield 56% relative to (3,5-dibromophenyl)trimethylsilane). NMR-^{1}H, δ, ppm: 0.35 (s, 9 H) 0.91 (t, *J*=7.32 Hz, 12 H) 1.19 - 1.47 (m, 18 H) 2.60 (d, *J*=6.41 Hz, 4 H), 7.26 (d, *J*=8.24 Hz 4 H (overlapped with $CHCl_3$)= 7.58 (d, *J*=7.94 Hz, 4 H) 7.73 (d, *J*=1.22 Hz 8 H) 7.77 (d, *J*=1.53 Hz 2 H) 7.87 (t, *J*=3.66 Hz 1 H). NMR-^{13}C, δ, ppm:-1.00, 10.79, 14.17, 23.06, 25.38, 28.85, 32.33, 39.72, 41.06, 126.60, 126.69, 127.31, 127.69, 129.66, 131.03, 137.86, 140.06, 140.18, 140.70, 141.19, 141.71. ESI-MS (TOF) m/z: [M+Na]+ calculated for $C_{49}H_{62}SiNa^+$ 701.4513, found: m/z [M+Na]+ 701.4501.

2.3. *Synthesis of 2-[4,4''-bis(2-ethylhexyl)[1,1':3'1''-terphenyl]-5'-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaboralane **(7)***

A solution of compound **5** (1.7 g, 3 mmol) and BBr_3 (2.9 g, 12 mmol) in carbon tetrachloride (40 ml) was boiled (95°C) with stirring for 14 hours. Ice was added to the mixture cooled to room temperature to safely neutralize excess BBr_3. The boronic acid was extracted with diethyl ether, and the solvent was removed using a rotary vacuum evaporator. Pinacol (0.34 g, 3 mmol) and benzene (45 ml) were added to the residue. The esterification was carried out on a rotary evaporator at 50°C and a pressure of 80 mbar until the solvent was completely removed. The product weight was 1.45 g (yield 95%). NMR-^{1}H, δ, ppm: 0.91 (t, *J*=7.32 Hz, 12 H) 1.21 - 1.44 (m, 30 H) 2.59 (d, *J*=7.02 Hz, 4 H) 7.24 (d, *J*=7.94 Hz, 4 H) 7.38 (s, 1 H) 7.61 (d, *J*=7.94 Hz, 3 H) 7.92 (s, 1 H) 8.02 (d, *J*=1.83 Hz, 2 H) NMR-^{13}C, δ, ppm: 10.79, 14.17, 23.05, 24.88, 25.37, 28.84, 32.29, 39.72, 41.08, 83.84, 126.98, 128.58, 129.48, 132.03, 138.35, 140.98. ESI-MS (TOF) m/z: [M+H]+ calculated for $C_{40}H_{57}BO_2H^+$ 581.4531, found: m/z [M+H]+ 581.4533.

2.4. *Synthesis of 2-[4,4''''-bis(2-ethylhexyl)[1,1':4',1'':3'',1''':4''',1''''-quinquehenyl]-5''-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**8**)*

A solution of compound **6** (1.18 g, 1.7 mmol) and BBr_3 (1.74 g, 7 mmol) in carbon tetrachloride (30 ml) was boiled with stirring for 14 hours. Ice was added to the mixture cooled to room temperature to safely neutralize excess BBr_3. The boronic acid was extracted with diethyl ether, and the extract was evaporated using a rotary vacuum evaporator. Pinacol (0.226 g, 1.9 mmol) and benzene (45 ml) were added to the isolated product. The esterification was carried out on a rotary evaporator at 50°C and a pressure of 80 mbar until the solvent was completely removed. Product weight 1.44 g (yield 94%). NMR-^{1}H, δ,ppm: 0.93 (t, *J*=7.32 Hz, 12 H) 1.18 - 1.47 (m, 30 H) 2.61 (d, *J*=6.41 Hz, 4 H) 7.25 (s, 2 H) 7.59 (d, *J*=8.24 Hz, 4 H) 7.67 - 7.85 (m, 8 H) 8.03 (m, 1 H) 8.12 (m, 2 H). NMR-^{13}C, δ, ppm: 10.78, 14.18, 23.05, 24.89, 25.35, 28.83, 32.30, 39.71, 41.05, 83.97, 126.67, 127.20, 127.31, 127.69, 128.57, 129.64, 132.34, 137.86, 139.58, 140.09, 140.70, 141.14. ESI-MS (TOF) m/z: [M+Na]+ calculated for $C_{52}H_{65}BO_2Na^+$ 755.4979, found: m/z [M+Na]+ 755.4959.

2.5. *Synthesis of 4,7-bis[4,4”-bis(2-ethylhexyl)-[1,1’:3’1”-terphenyl]-5’-yl]-2,1,3-benzothiadiazole)* ***(9)***

A mixture of compound **7** (1.71 g, 2.94 mmol) and 4,7-dibromo-2,1,3-benzothiadiazole (0.318 g, 1.1 mmol), $Pd(PPh_3)_4$ (0.12 g, 0.1 mmol), toluene (40 ml), Na_2CO_3 (2 ml, 2M aq.) and ethanol (2 ml) were boiled with stirring for 36 hours. Extraction of the product was carried out with toluene, and purification using column chromatography on silica gel (eluent - a mixture of petroleum ether-toluene 5:1 vol.). The mass of the product was 0.50 g (yield 53% relative to **7**). NMR-^{1}H, δ, ppm: 0.83 - 1.04 (m, 24 H) 1.21 - 1.49 (m, 36 H) 2.63 (d, *J*=6.41 Hz, 8 H) 7.30 (d, *J*=8.24 Hz, 8 H) 7.69 (d, *J*=8.24 Hz, 8 H) 7.93 (t, *J*=3.04 Hz 2 H) 7.95 (s, 2 H) 8.19 (d, *J*=1.53 Hz, 4 H). NMR-^{13}C, δ, ppm: 10.85, 14.06, 23.06, 25.69, 29.01, 32.6, 39.97, 41.23, 125.92, 126.8, 127.13, 128.23, 129.71, 133.72, 138.34, 138.51, 141.41, 142.16, 154.39. ESI-MS (TOF) m/z: [M+H]+ calculated for $C_{74}H_{92}N_2SH^+$ 1041.7054, found: m/z [M+H]+ 1041.7032

2.6. *Synthesis of 4,7-bis[4,4””-bis(2-ethylhexyl)[1,1’:4’,1”:3”,1”’:4”’,1””-quinquephenyl]-5”-yl)-2,1,3-benzothiadiazole* ***(10)***

A mixture of compound **8** (1.15 g, 1.4 mmol), 4,7-dibromo-2,1,3-benzothiadiazole (0.156 g, 0.5 mmol), $Pd(PPh_3)_4$ (0.045 g, 0.04 mmol), toluene (20 ml), Na_2CO_3 (2 ml, 2M aq.) and ethanol (2 ml) were boiled with stirring for 24 hours. The product was extracted with toluene. Purification was carried out using silica gel column chromatography. Eluent: petroleum ether-toluene (volume ratio 2:1). Product weight: 0.265 g (yield 28% relative to **8**). NMR-^{1}H, δ, ppm: 0.84 - 1.00 (m, 24 H) 1.23 - 1.39 (m, 34 H) 1.44 (s, 2 H) 2.61 (d, *J*=6.71 Hz, 8 H) 7.25-7.30 (m, 8 H (overlapped with $CHCl_3$)) 7.57 (d, *J*=7.94 Hz, 8 H) 7.81 (dd, J_1=8.40 Hz, J_2=23.32 Hz, 16 H) 8.01 (m, 4 H) 8.25 (m, 4 H). NMR-^{13}C, δ, ppm: 10.85, 14.05, 23.06, 25.70, 29.01, 32.60, 39.97, 41.22, 126.78, 127.16, 127.46, 127.78, 129.73, 133.71 138.01, 139.75, 140.63, 141.34, 141.96, 154.42. ESI-MS (TOF) m/z: [M]+ calculated for $C_{98}H_{108}N_2S^+$ 1344.8228, found: m/z 1342.9241 for $C_{98}H_{106}N_2S$ $[M-2H]^+$.

3. NMR spectra of the synthesized compounds

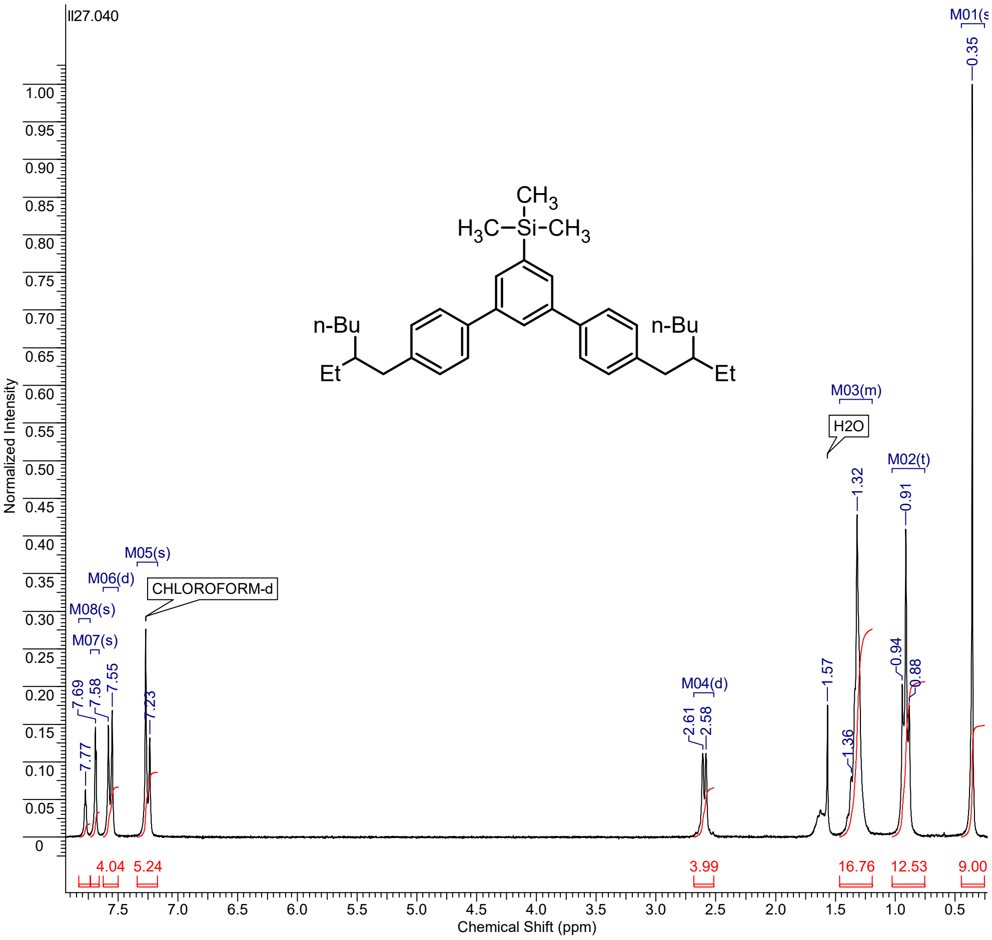


Figure S1. NMR-^{1}H spectrum of compound **5**.

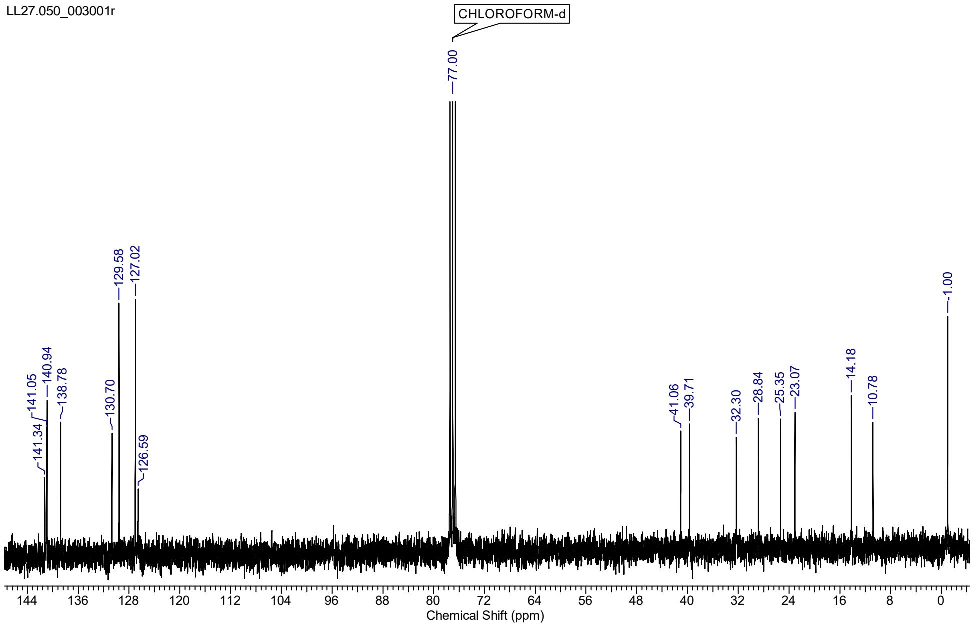


Figure S2. NMR-^{13}C spectrum of compound **5**.

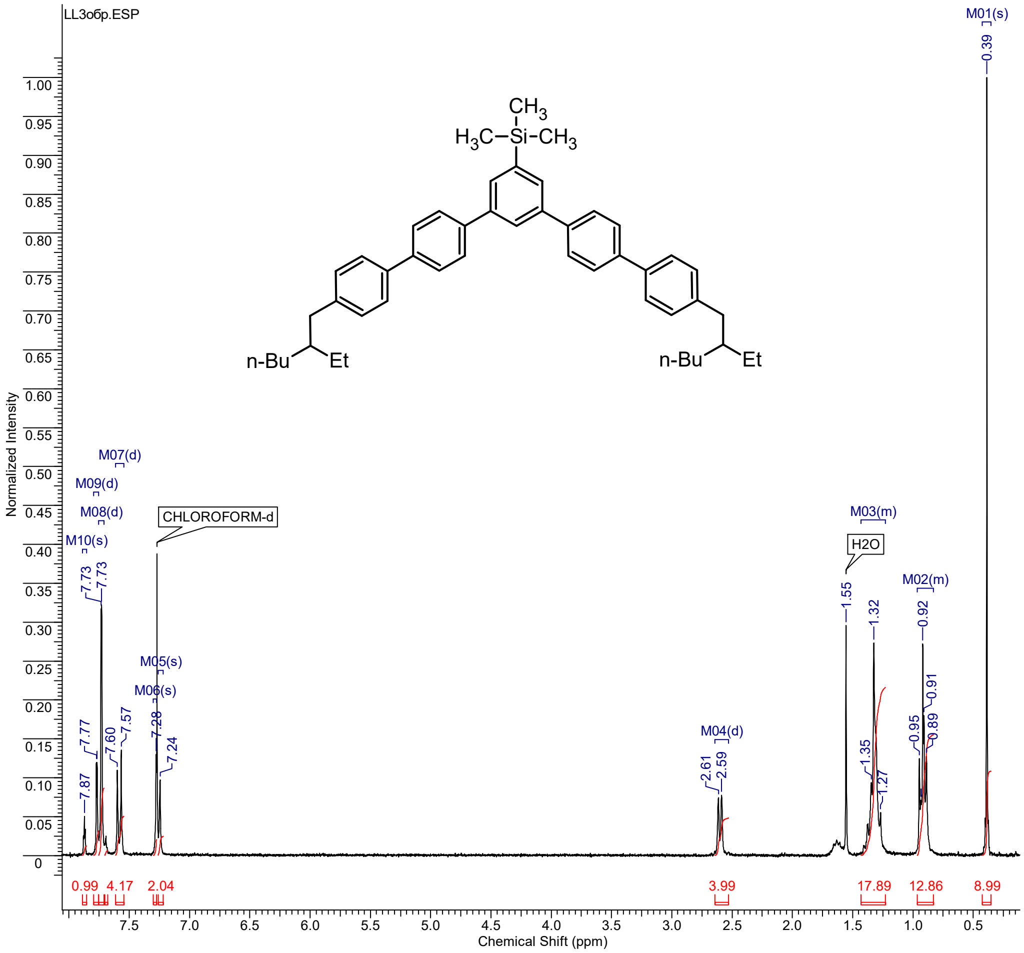


Figure S3. NMR-^{1}H spectrum of compound **6**.

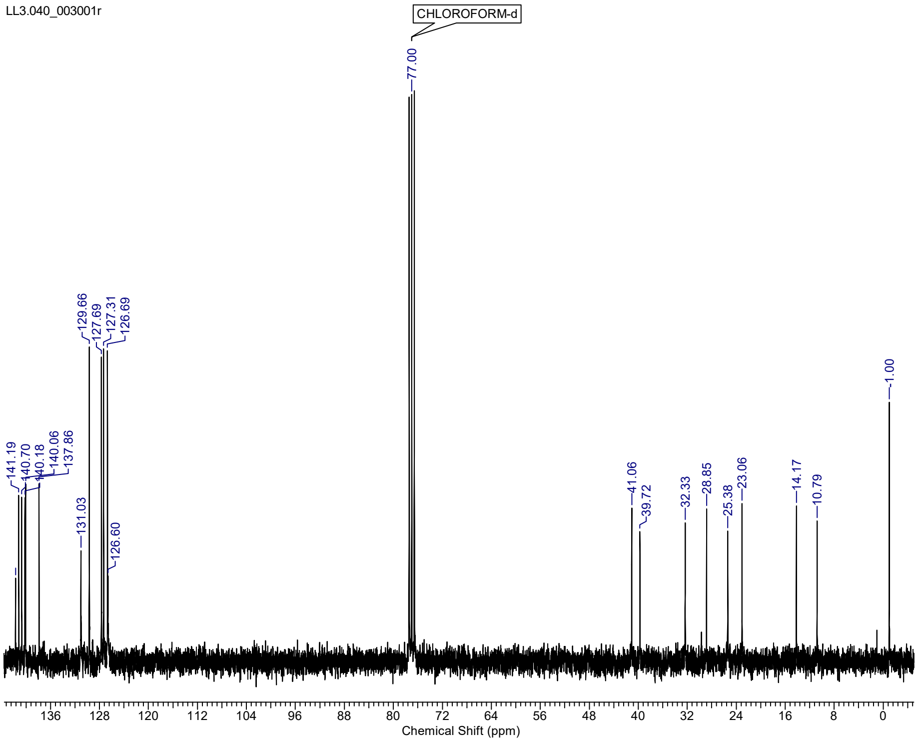


Figure S4. NMR-^{13}C spectrum of compound **6**.

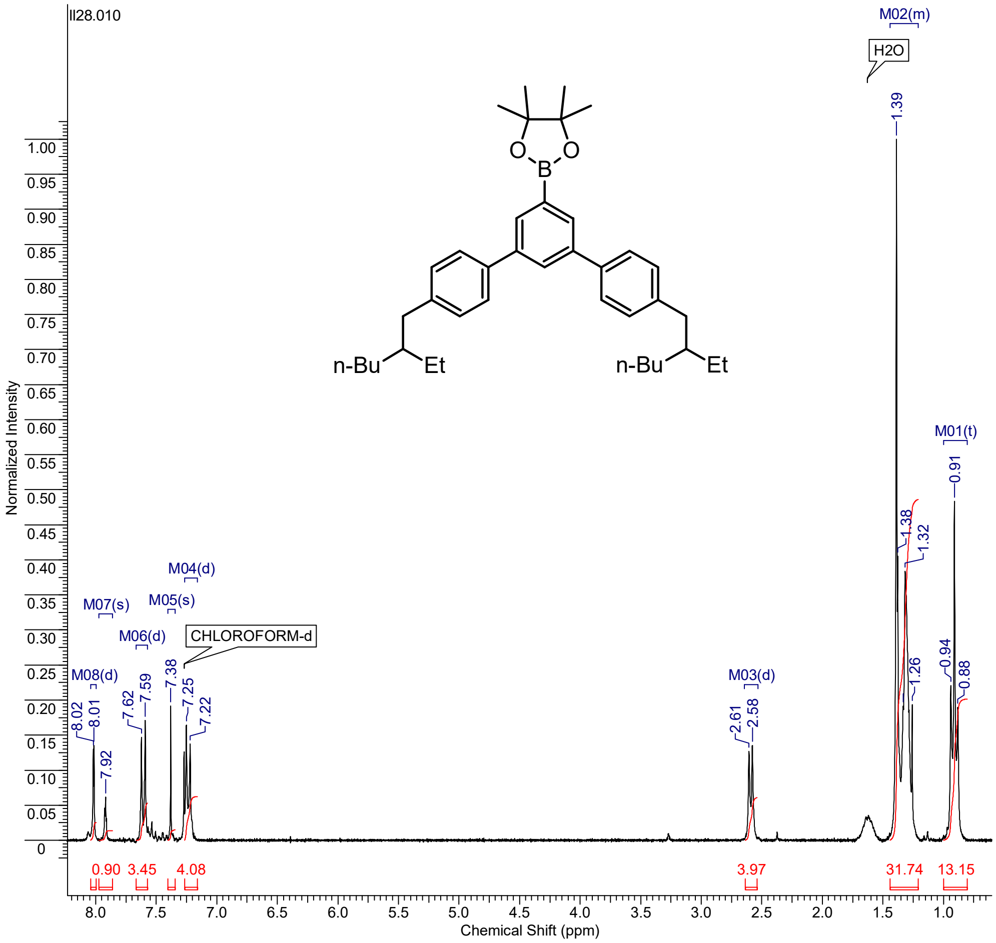


Figure S5. NMR-^{1}H spectrum of compound **7.**

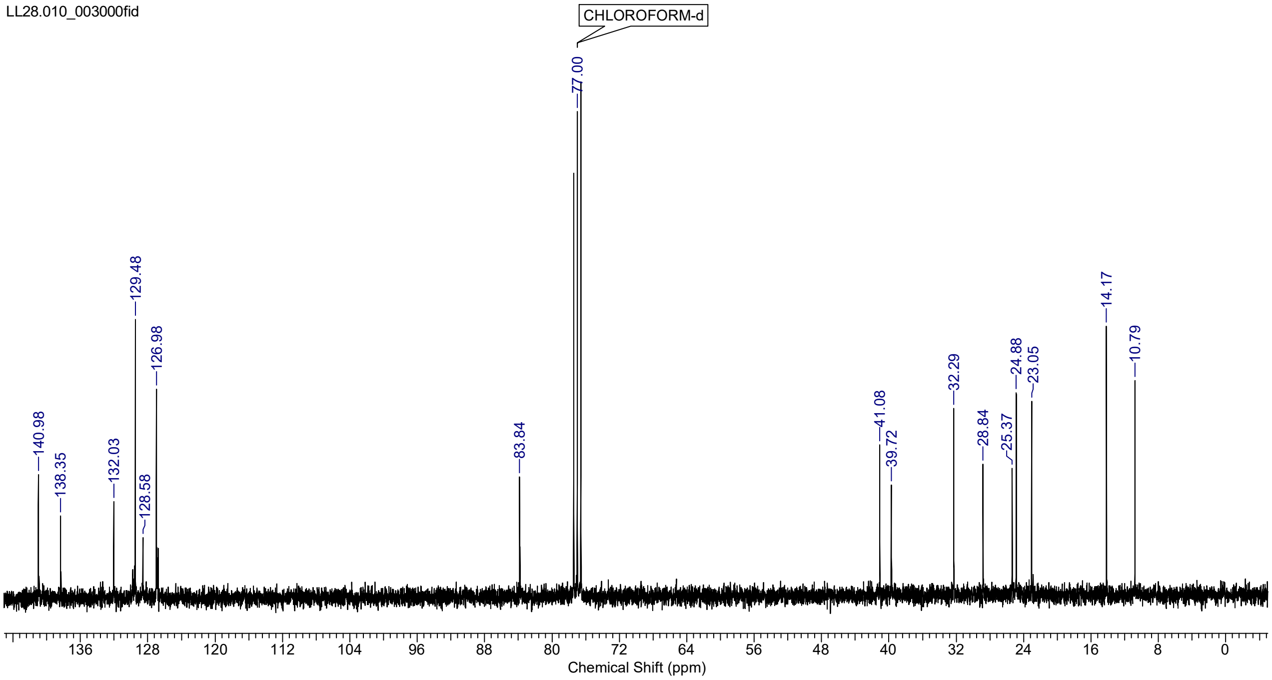


Figure S6. NMR-^{13}C spectrum of compound **7.**

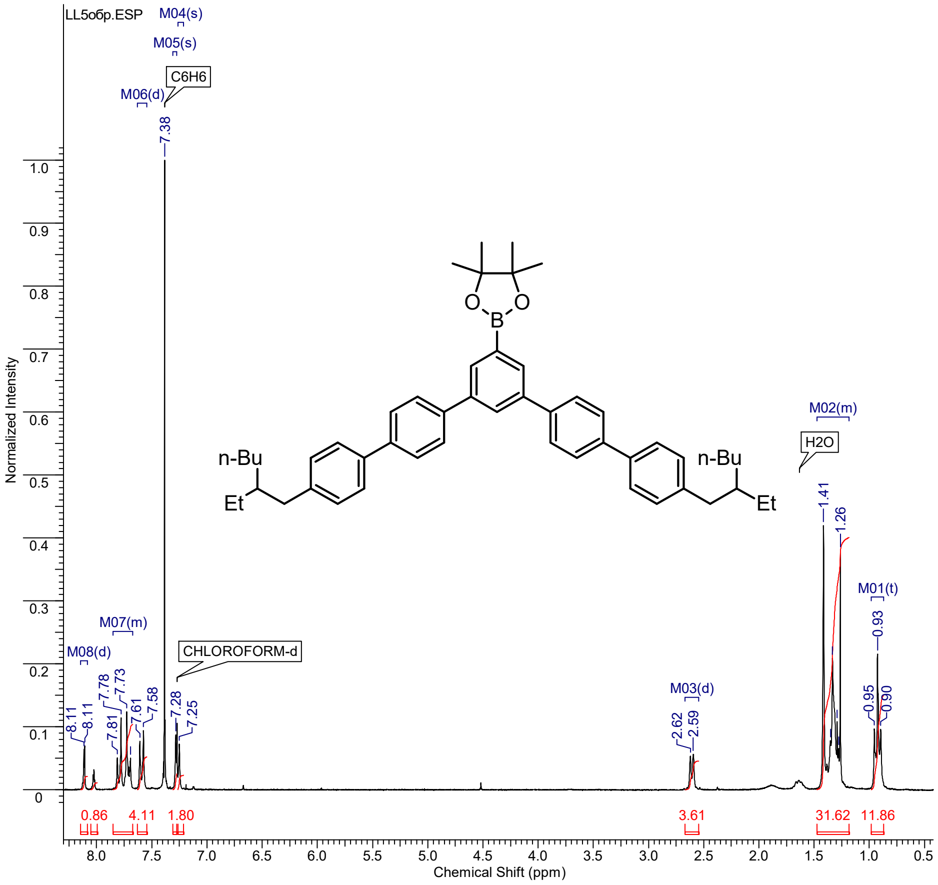


Figure S7. NMR-^{1}H spectrum of compound **8**.

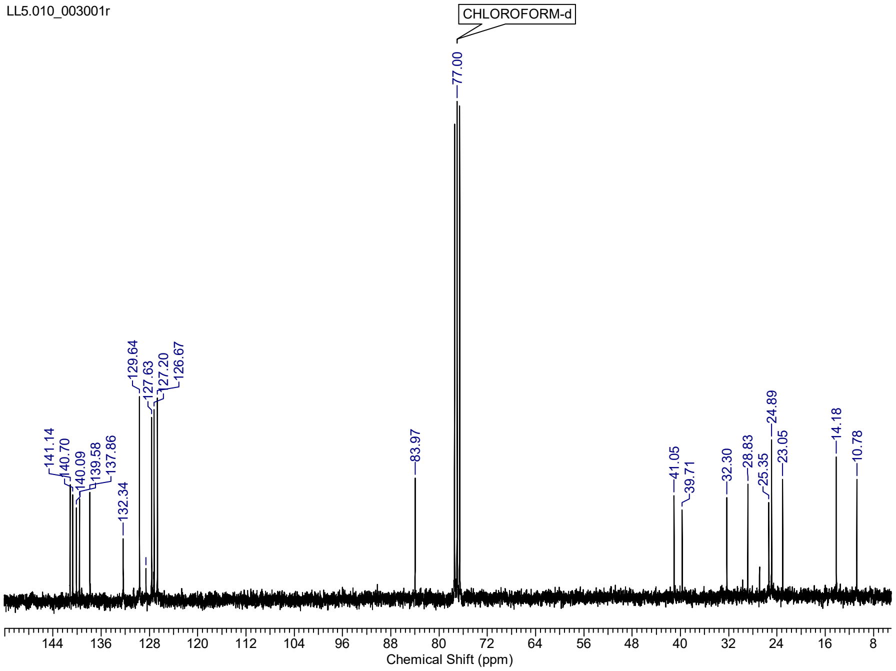


Figure S8. NMR-^{13}C spectrum of compound **8**.

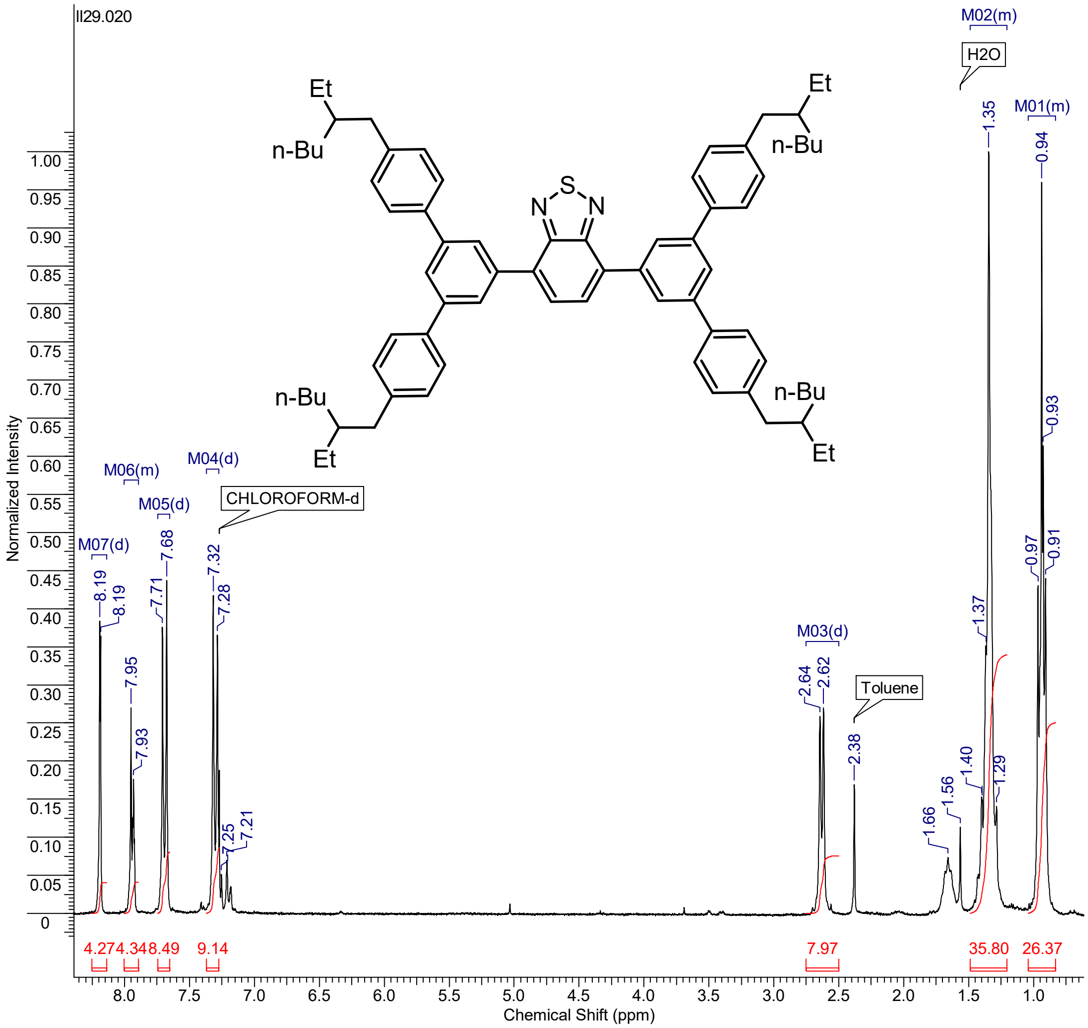


Figure S9. NMR-^{1}H spectrum of **9**.

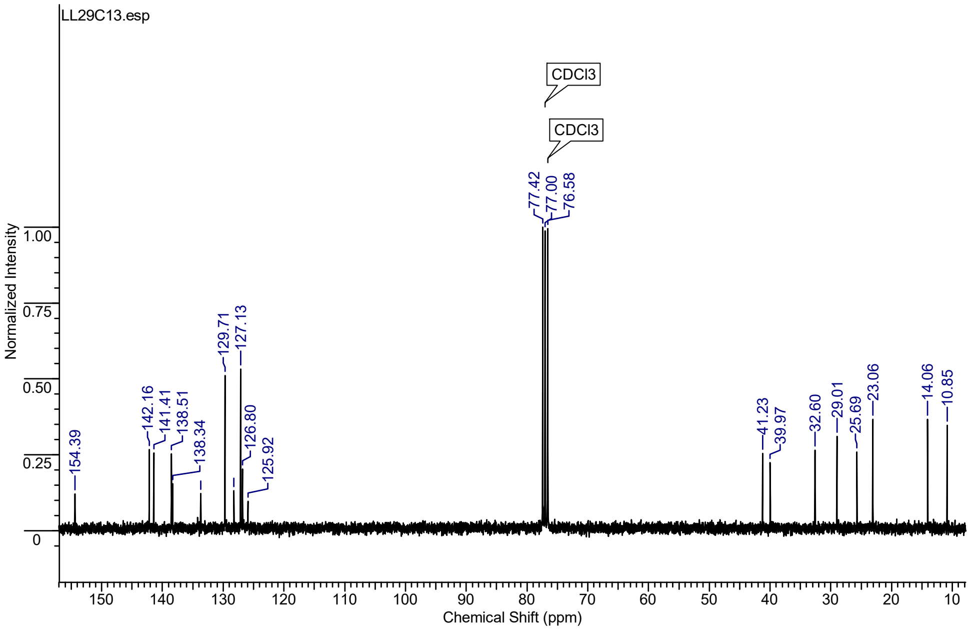


Figure S10. NMR-^{13}C spectrum of **10**.

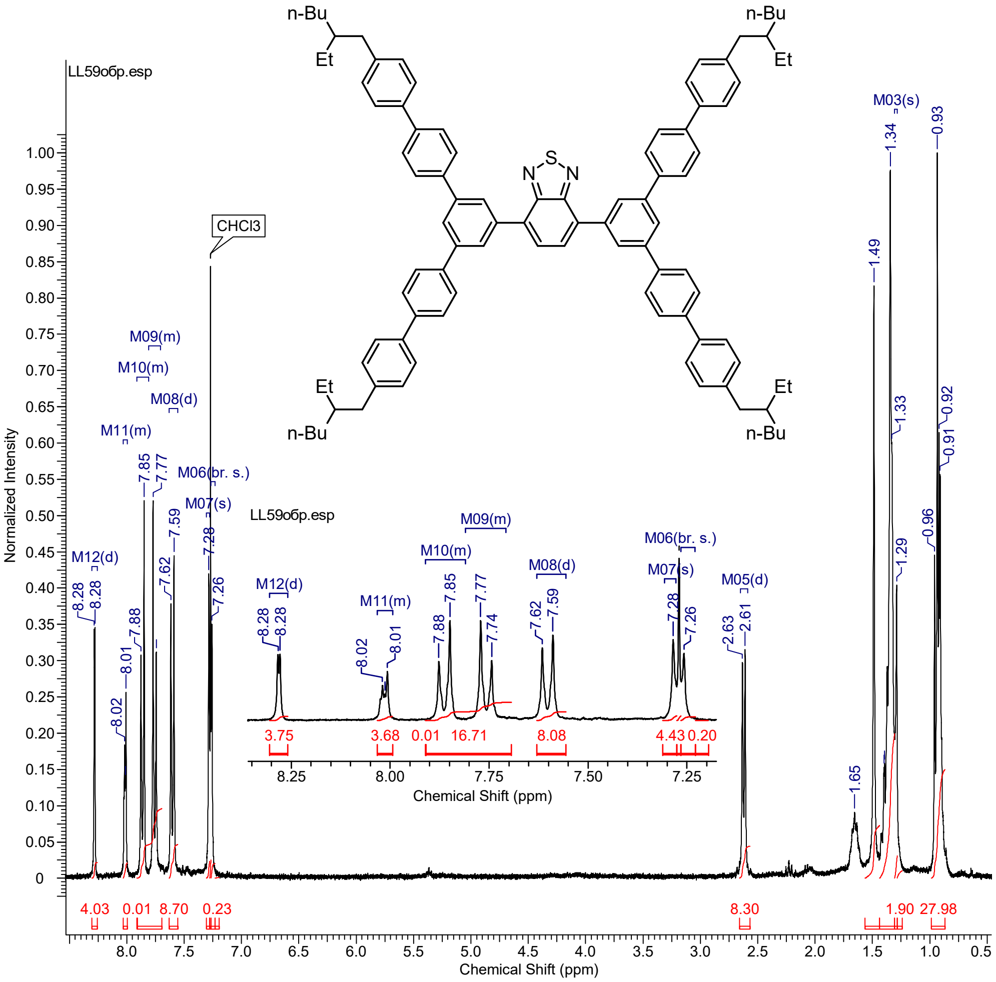


Figure S11. NMR-^{1}H spectrum of **10**.

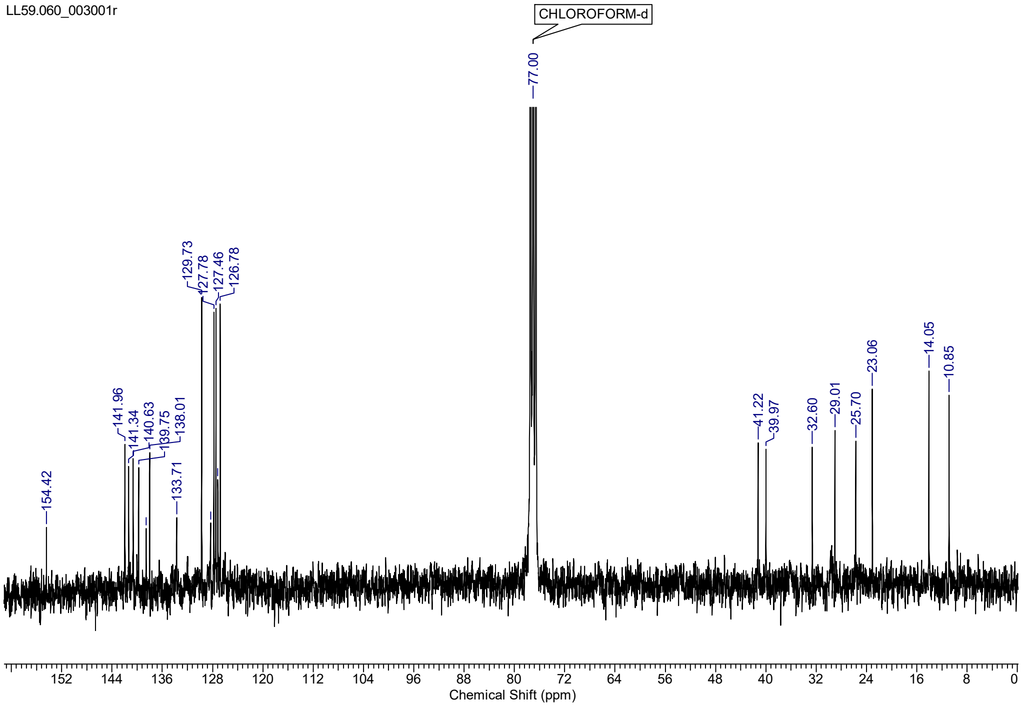


Figure S12. NMR-^{13}C spectrum of **10**.

4. Fluorescence spectra of diluted solutions of 9 and 10

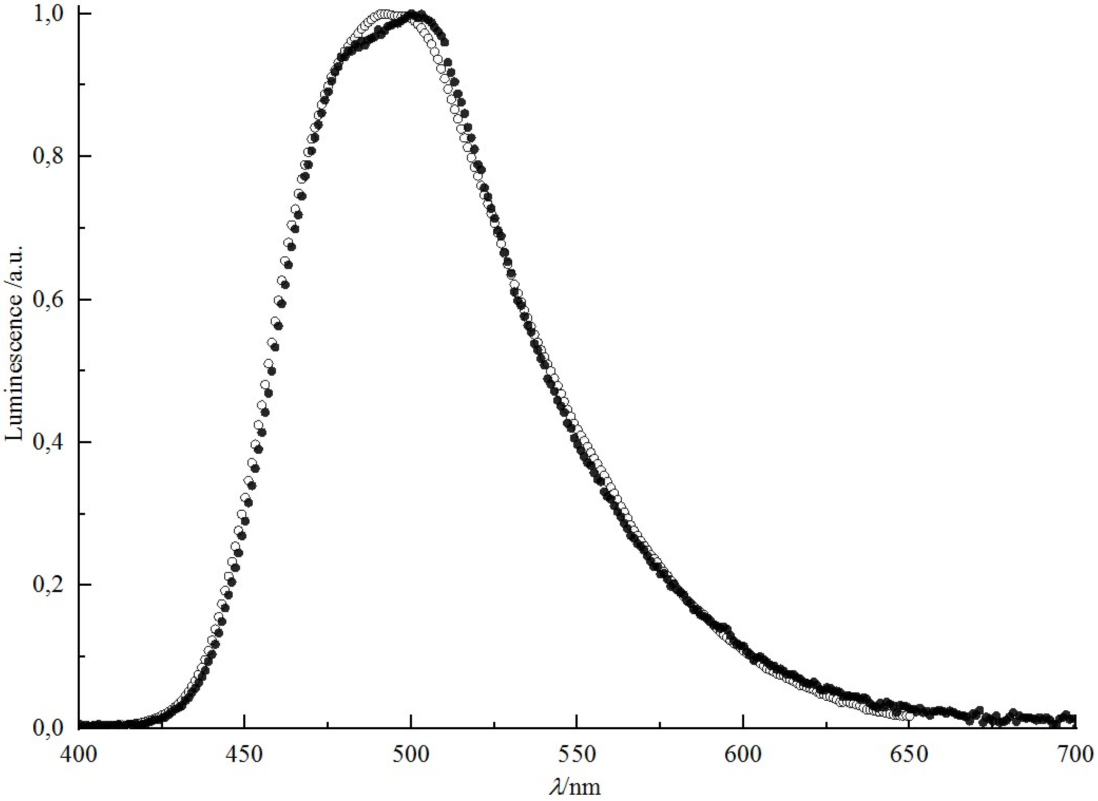


Figure S13. Fluorescence spectra of diluted solutions in THF of compounds **9** (●) (λ_{exc}=388 nm) and **10** (○) (λ_{exc}=386 nm).

5. Thermal properties of 9 and 10

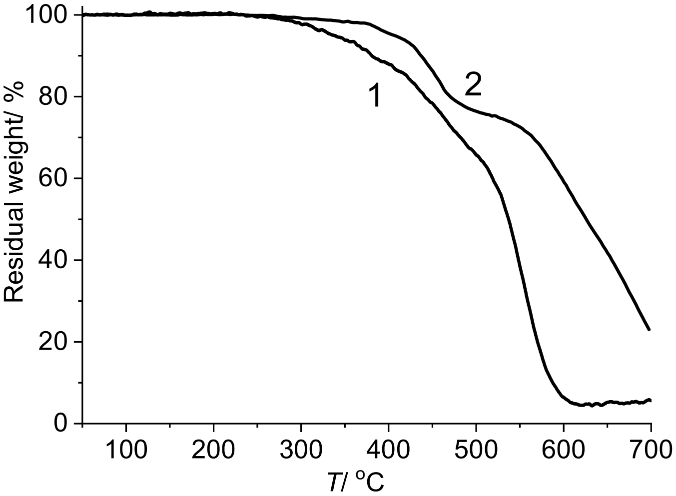


Figure S14. TGA curves in air of **9** (*1*) and **10** (*2*) luminophores.

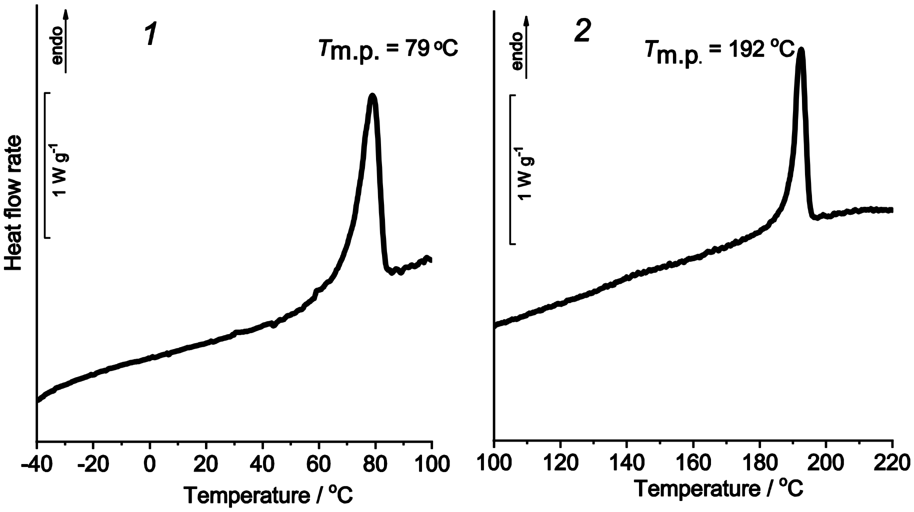
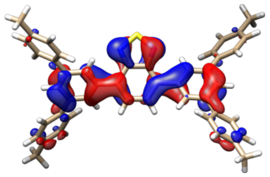


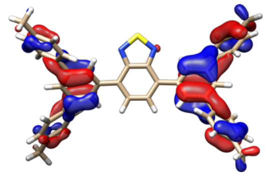
Figure S15. DSC curves of the first heating of **9** (*1*) and **10** (*2*) luminophores.

6. **Frontier molecular orbitals of the investigated luminophores**

Occupied



#157 HOMO-13



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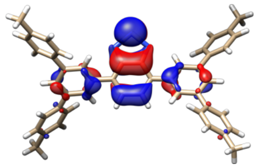

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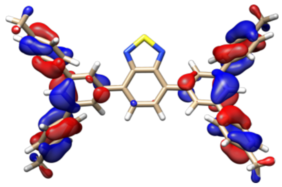

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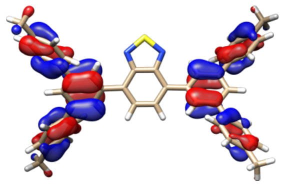

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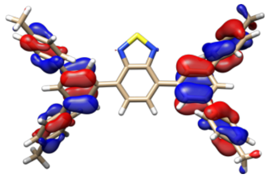

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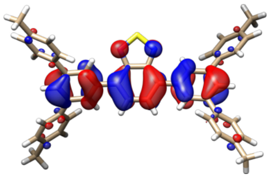
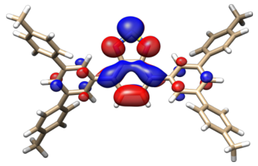
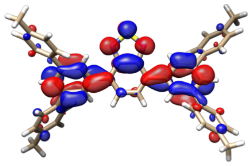


#170 HOMO

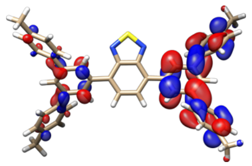
Vacant



#171 LUMO



#172 LUMO+1



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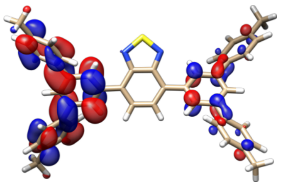
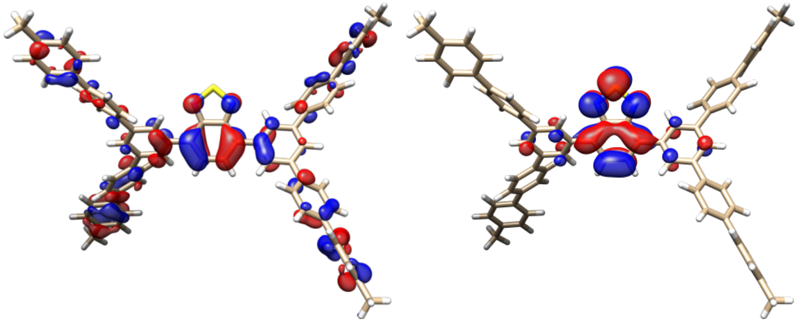


#174 LUMO+3

Figure S16. Frontier molecular orbitals of compound **9**.

Occupied **Vacant**



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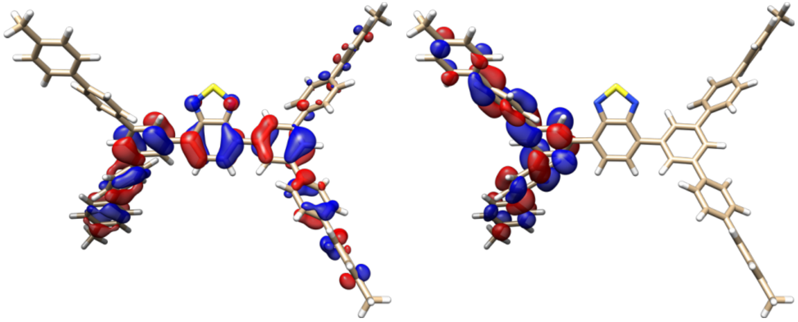
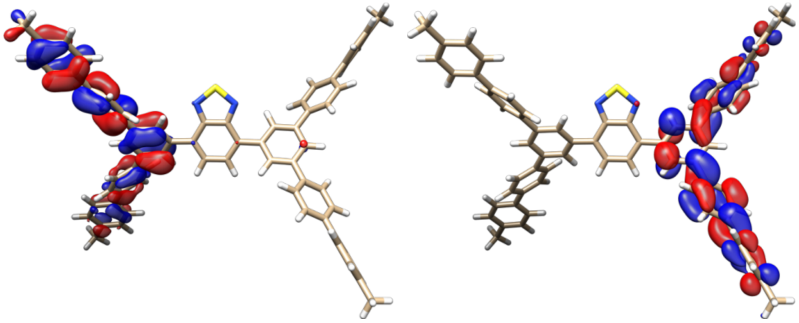


#248 HOMO-2 #252 LUMO+1



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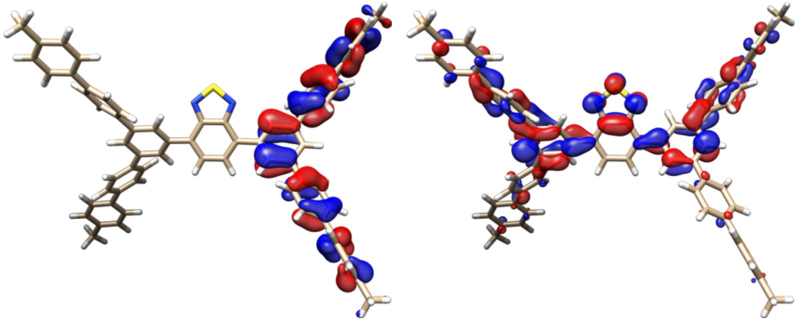

#250 HOMO #254 LUMO+3

Figure S17. Frontier molecular orbitals of compound **10**.

7. **Calculated characteristics of main electronic transitions of luminophores**

Table S1. Characteristics of main electronic transitions of compound **9**.

Transition	**Energy (cm^{-1})**	**Wavelength (nm)**	**Oscillator strength**		**Orbitals (from GS)**
			(electric)	**(velocity)**	
1	25547	391.4	0.44504	0.08072	170 -> 171
2	26219	381.4	0.00490	0.00035	
3	26290	380.4	0.00425	0.00065	
4	28997	344.9	0.00164	0.00111	
5	30877	323.9	0.08442	0.01802	
6	34365	291.0	0.00005	0.00006	
7	34377	290.9	0.00007	0.00008	
8	35243	283.7	0.00010	0.00017	
9	35248	283.7	0.00007	0.00005	
10	35635	280.6	0.00003	0.00332	
11	35938	278.3	0.00666	0.00334	
12	35983	277.9	0.00465	0.00167	
13	36982	270.4	1.11647	0.58195	170 -> 172
14	37584	266.1	0.11936	0.01809	160 -> 171
15	38030	262.9	0.00320	0.00511	
16	38985	256.5	0.07136	0.02347	
17	39319	254.3	0.21618	0.05390	169 -> 172
18	39782	251.4	0.12143	0.01733	158 -> 171
19	39958	250.3	0.05944	0.01216	
20	40132	249.2	0.08604	0.00349	
21	40535	246.7	0.03735	0.03657	
22	40615	246.2	0.31893	0.23468	157 -> 171 168 -> 174
23	41010	243.8	0.02807	0.00213	
24	41055	243.6	0.14560	0.05004	167 -> 173

Table S2. Characteristics of main electronic transitions of compound **10**.

Transition	**Energy (cm^{-1})**	**Wavelength (nm)**	**Oscillator strength**		**Orbitals (from GS)**
			(electric)	**(velocity)**	
1	25057	399.1	0.01057	0.00102	
2	25147	397.7	0.00767	0.00046	
3	25312	395.1	0.44451	0.11918	248 -> 251
4	26916	371.5	0.00063	0.00050	
5	28102	355.8	0.21998	0.07448	246 -> 251
6	33173	301.4	0.00698	0.00657	
7	33462	298.8	0.00721	0.00740	
8	33654	297.1	0.00038	0.00054	
9	34507	289.8	0.04666	0.01647	
10	34560	289.4	0.02942	0.00915	
11	34695	288.2	0.00081	0.00070	
12	34699	288.2	0.00102	0.00071	
13	35499	281.7	1.59899	0.91271	249 -> 252 250 -> 253
14	35564	281.2	0.01181	0.00647	
15	35572	281.1	0.02223	0.01222	
16	35651	280.5	0.00664	0.00413	
17	35656	280.5	0.00308	0.00204	
18	35785	279.4	1.69167	0.82172	249 -> 254
19	35822	279.2	1.90353	0.93967	250 -> 254
20	36231	276.0	0.00136	0.00081	
21	36237	276.0	0.00081	0.00049	
22	36648	272.9	0.02556	0.00074	
23	37030	270.1	0.03748	0.05522	
24	37260	268.4	0.01537	0.01414	

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