Supporting Information

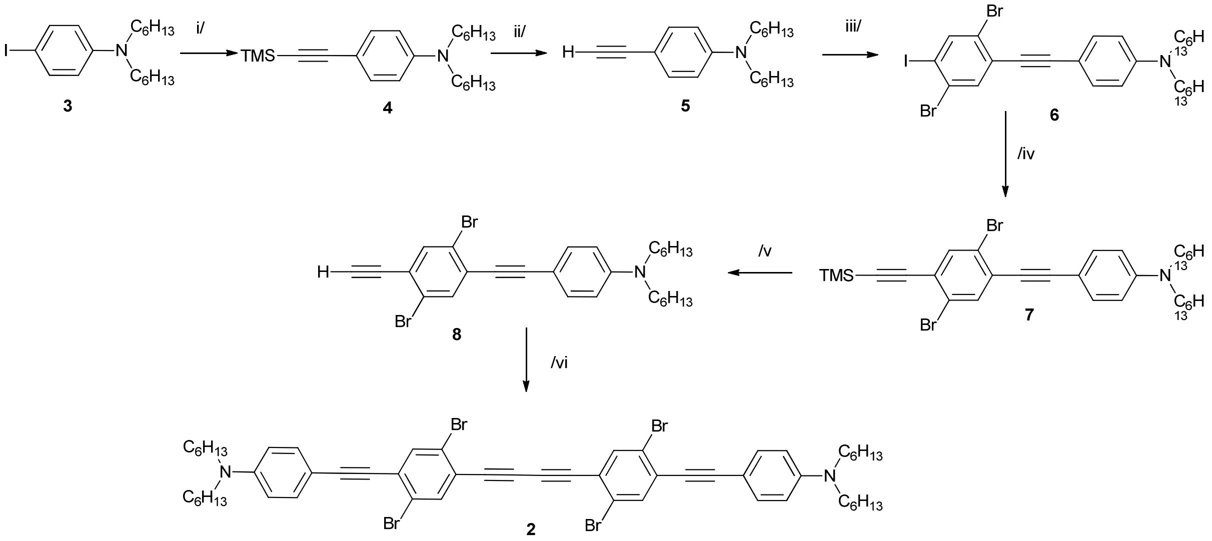
General procedures

All reactions were routinely performed under argon. THF was dried and degassed on a solvent station by passage through an activated alumina column followed by argon flush. Other solvents were used without further purification. All reagents were purchased from Sigma Aldrich®, Acros® or Alfa Aesar® with the best available quality grade. NMR spectra (^{1}H, ^{13}C) were recorded at 298K on a BRUKER® AC 200 operating at 200.13 and 50.32 MHz for ^{1}H and ^{13}C respectively and on a BRUKER® 500 Ultra Shield operating at 500.1 and 126.3 MHz for ^{1}H and ^{13}C respectively. Data are listed in parts per million (ppm) and are reported relative to tetramethylsilane (^{1}H, ^{13}C), residual solvent peaks being used as internal standard ($CHCl_3$ ^{1}H: 7.26 ppm, ^{13}C: 77.36 ppm). UV-visible spectra were recorded on a Jasco® V-670 spectrophotometer in diluted dichloromethane solutions. Luminescence spectra were measured using a Horiba-Jobin-Yvon Fluorolog-3® spectrofluorimeter, equipped with a three-slit double-grating excitation and emission monochromator with dispersions of 2.1 nm.mm-1 (1200 grooves mm^{-1}). In the visible range [400-845 nm] the R928 detector was used. Spectra were reference corrected for both the excitation source light intensity variation (lamp and grating) and the emission spectral response (detector and grating). Fluorescence quantum yields Q were measured in diluted dichloromethane solution with an optical density lower than 0.1 with an excitation wavelength at 410 nm, using the relative methodology based on the following equation:

$$Q_x/Q_r = [A_r(\lambda)/A_x(\lambda)][n_x^2/n_r^2][D_x/D_r]$$

where A is the absorbance at the excitation wavelength (λ), n the refractive index and D the integrated luminescence intensity. “r” and “x” stand for reference and sample. Here, references is coumarine 153 in MeOH (Q_r = 0.45). Singlet-oxygen phosphorescence were recorded using a liquid nitrogen cooled, solid Indium/Gallium/Arsenic detector (850-1600 nm), and singlet oxygen generation quantum yield were deduced from an analogous methodology as for Fluorescence quantum yields (see above) using phenalenone as a reference ($\phi_\Delta = 0.95$ in CH_2Cl_2). Excitation of reference and sample compounds in dichloromethane was performed at the same wavelength (410 nm). TPA cross-section spectra were obtained by two-photon excited fluorescence measurement of diluted dichloromethane solutions of the compound using a Ti:sapphire femtosecond laser in the range 700-900 nm. The excitation beam (5 mm diameter) was focalised with a lens (focal length 10 cm) at the middle of the fluorescence cell (10 mm). The fluorescence, collected at 90° to the excitation beam, was focused into an optical fiber (diameter 600 μm) connected to an Ocean Optics S2000 spectrometer. The incident beam intensity was adjusted to 50 mW in order to ensure an intensity-squared dependence of the fluorescence over the whole spectral range. The detector integration time was fixed to 1 s. Calibration of the spectra was performed by comparison with the published 700-900 nm Coumarin-307 and fluorescein two photon absorption spectra. The measurements were done at room temperature in dichloromethane and at a concentration *ca* 10^{-4} or 10^{-5} M. HRMS measurements were performed either by ESI-TOF or MALDI TOF. In the case of ESI-TOF a Bruker Daltonics ® Micro TOF-Q II was used with a resolution of 8000, in positive mode with a capillary tension of 4500V, a source temperature of 180°C, and a cone tension of 60V. The internal reference used for calibration was sodium formate. In the case of MALDI-TOF a Bruker Daltonics ® Ultraflex III was used with a solid YAG Laser, in positive reflectron mode. Dithranol was used as a matrix for all samples.

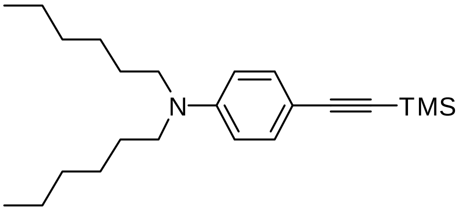
Synthetic scheme



(i) TMSA, THF / Et_3N, $Pd(PPh_3)_2Cl_2$ (0.02eq), CuI (0.06eq) 12H, 55°C (ii) K_2CO_3 (3 eq), THF / MeOH (1 : 1) (iii) THF / Et_3N, $Pd(PPh_3)_2Cl_2$ (0.02eq), CuI (0.04eq) 12H, RT (iv) TMSA, THF / Et_3N, $Pd(PPh_3)_2Cl_2$ (0.02eq), CuI (0.06eq) (V) K2CO3 (3 eq), THF / MeOH (1 : 1) (vi) THF/ Et_3N, $Pd(PPh_3)_2Cl_2$ (0.01eq), CuI (0.01eq) 12H, RT

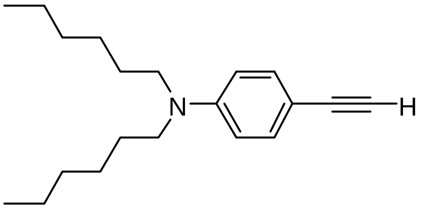
Synthetic procedures

N,N-dihexyl-4-((trimethylsilyl)ethynyl)aniline (4)



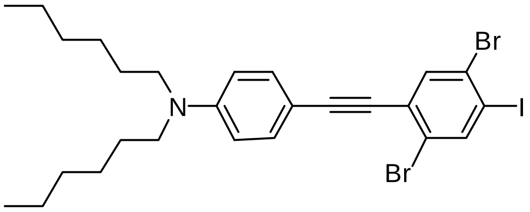
N,N-dihexyl-4-iodoaniline **3** (9.1 g, 23.5 mmol) and TMSA (4.3 mL, 30.5 mmol) were dissolved in a Et_3N/THF mixture (V/V = 60/60 mL). The solution was degassed by bubbling argon for 10 min. $Pd(PPh_3)_2Cl_2$ (165 mg) and CuI (134 mg) were added. The solution was stirred overnight at 55°C. After cooling to room temperature, ethyl acetate was added. The organic layer was washed with a solution of saturated ammonium chloride, water and brine. After drying on anhydrous Na_2SO_4, the solution was filtered, and solvents were removed under reduced pressure (8.6 g, 100 %). ^1H NMR (200 MHz $CDCl_3$) δ ppm 7.25 (d, J = 9.2 Hz, 2H), 6.53 (d, J =9.2 Hz, 2H), 3.26 (t, J = 7.7 Hz, 4 H), 1.52 (m, 4H), 1.32 (m, 12H), 0.90 (t, 3J=6.62 Hz, 6 H), 0.22 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ ppm 148.64, 133.42, 111.43, 108.73, 107.16, 91.00, 51.25, 32.11, 27.52, 27.14, 23.08, 14.20, 0.29.

4-ethynyl-N,N-dihexylaniline (5)



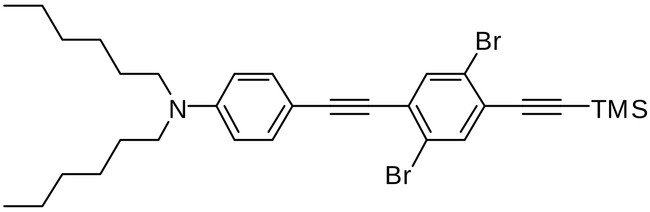
A solution of **4** (8.6 g, 24 mmol) in a methanol/THF mixture (V/V = 150/150 mL) was treated with K_2CO_3 (9.9 g, 72 mmol). The mixture was stirred for 2h at room temperature and then concentrated under reduced pressure. It was solubilised in petroleum ether and washed with water and brine. After drying on anhydrous Na_2SO_4, the solution was filtered, and solvents were removed under reduced pressure to provide a brown oil (4.5 g, 65 %), which was not further purified due to relative instability of the compound, and only characterized by ^{1}H NMR before being engaged in the next step. ^{1}H NMR (200 MHz, $CDCl_3$) : δ 7.30 (d, J = 9.0 Hz, 2H), 6.50 (d, J = 9.0 Hz, 2H), 3.23 (t, J = 7.5 Hz, 4H), 2.93 (s, 1H), 1.55 (m, 4H), 1.29 (m, 12H), 0.88 (t, J = 6.5 Hz, 6H).

4-((2,5-dibromo-4-iodophenyl)ethynyl)-N,N-dihexylaniline (6)



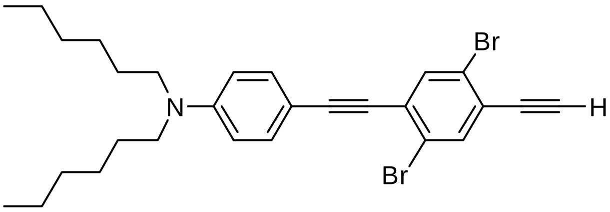
Aniline **5** (1.46 g, 5.1 mmol) and 1,4-dibromo-2,5-diiodobenzene (4.6 g , 9.4 mmol) were dissolved in a Et_3N/THF mixture (V/V = 40/40 mL). The solution was degassed by bubbling argon for 10 min. $Pd(PPh_3)_2Cl_2$ (72 mg) and CuI (39 mg) were added. The solution was stirred overnight at room temperature. Ethyl acetate was added. The organic layer was washed with a solution of saturated ammonium chloride, water and brine. After drying on anhydrous Na_2SO_4, the solution was filtered, and solvents were removed under reduced pressure. The crude material was purified by flash chromatography on silica gel (cyclohexane and then cyclohexane / dichloromethane : 98/2, then 65/35, then 60/40). The product was recrystallized in a mixture ether/dichloromethane, then washed with petroleum ether and finally with cyclohexane (1.4g, 27%). ^{1}H NMR (200 MHz, $CDCl_3$) δ ppm 8.04 (s, 1 H), 7.72 (s, 1 H), 7.38 (d, J = 8.8 Hz, 2 H), 6.55 (d, J = 8.8 Hz, 2 H), 3.28 (t, J = 7.6 Hz, 4 H), 1.57 (m, 4 H), 1.32 (s, 12 H), 0.89 (m, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 148.70, 142.50, 135.17, 133.35, 128.21, 128.15, 123.90, 111.28, 107.47, 99.43, 98.86, 84.84, 51.11, 31.84, 27.31, 26.91, 22.83, 14.20. HRMS (ESI) calcd. for $[M+H]^+$ 645,9946, found 645.9982.

4-((2,5-dibromo-4-((trimethylsilyl)ethynyl)phenyl)ethynyl)-N,N-dihexylaniline (7)



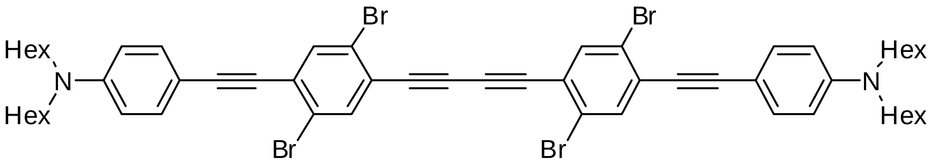
Compound **6** (500 mg, 0.77 mmol) and TMSA (0.14 mL, 1.0 mmol) were dissolved in Et_3N (V = 10 mL). The solution was degassed by bubbling argon for 10 min. $Pd(PPh_3)_2Cl_2$ (10 mg) and CuI (6 mg) were added. The solution was stirred overnight at room temperature. Ethyl acetate was added. The organic layer was washed with a solution of saturated ammonium chloride, water and brine. After drying on anhydrous Na_2SO_4, the solution was filtered, and solvents were removed under reduced pressure. The crude material was purified by flash chromatography on silica gel (petroleum ether) to provide the expected product as a yellowish oil, (240 mg, 50 %). ^{1}H NMR (200 MHz, $CDCl_3$) δ ppm 7.66 (b, 2H), 7.37 (d, J = 9 Hz, 2H), 6.55 (d, J = 9 Hz, 2H), 3.26 (t, J = 7.6 Hz, 4H), 1.52 (m, 4H), 1.30 (m, 12H), 0.88 (t, J = 6.5 Hz, 6H), 0.25 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$) δ ppm 149.39, 137.09, 136.06, 134.11, 128.68, 125.61, 124.51, 123.76, 111.92, 108.18, 100.12, 93.00, 92.42, 86.05, 51.73, 32.45, 27.92, 23.43, 14.78, 0.27. HRMS (MALDI) m/z, calcd for $[M]^+$ 613.1375, found 613.1370

4-((2,5-dibromo-4-(ethynyl)phenyl)ethynyl)-N,N-dihexylaniline (8)



A solution of compound **7** (235 mg, 0.38 mmol) in a methanol/THF mixture (V/V = 15/15 mL) was treated with K_2CO_3 (157 mg, 1.14 mmol). The mixture was stirred for 2h at room temperature and then concentrated under reduced pressure. It was solubilized in ethyl acetate and washed with water and brine. After drying on anhydrous Na_2SO_4, the solution was filtered, and solvents were removed under reduced pressure to provide a yellow oil (206 mg, 100 %). Owing to relative instability of the product, it was engaged in the next step **without additional purification, and a sample was characterised only by ^{1}H NMR**. ^{1}H NMR (200 MHz, $CDCl_3$) : δ 7.69 (s, 1H), 7.67 (s, 1H), 7.37 (d, J = 8.9 Hz, 2H), 6.55 (d, J = 9.0 Hz, 2H), 3.44 (s, 1H), 3.26 (t, J = 7.5 Hz, 4H), 1.53 (m, 4H), 1.30 (m, 12H), 0.88 (t, J = 6.5 Hz, 6H).

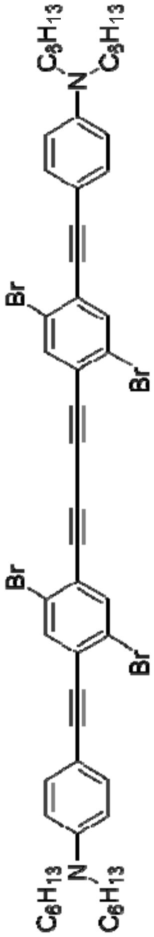
Chromophore 2

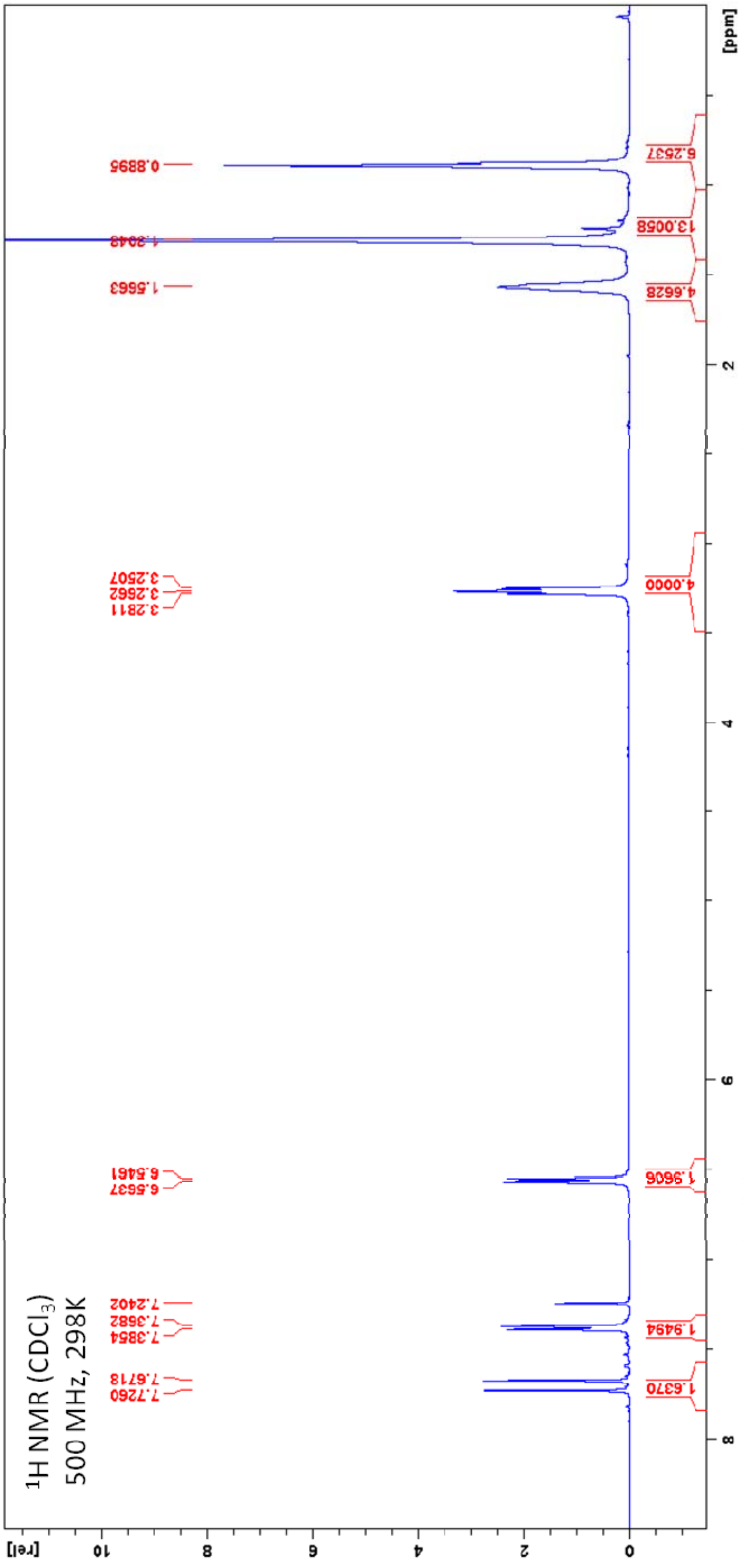


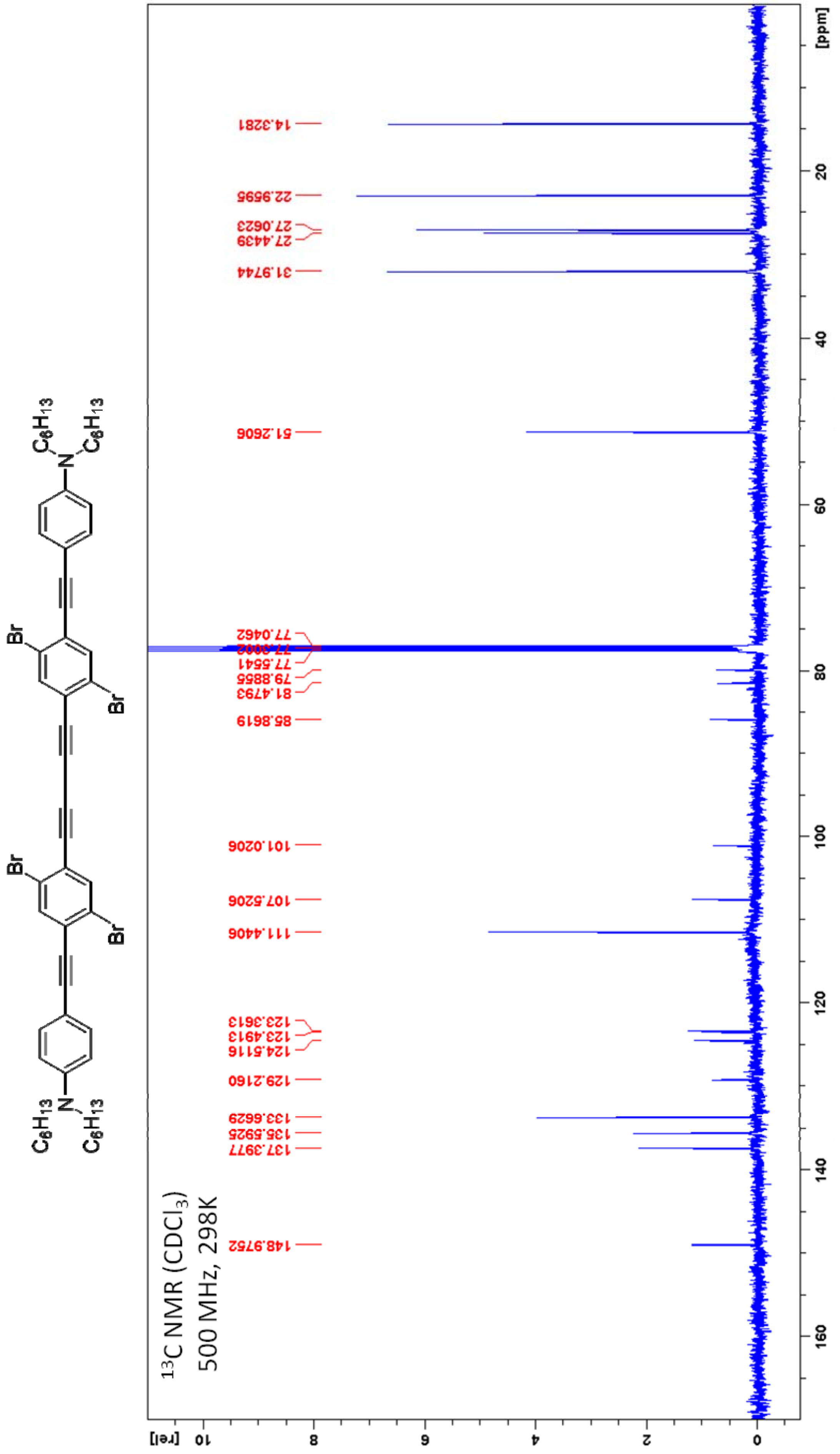
Compound **8** (70 mg, 0.13 mmol) was dissolved in a Et_3N/THF mixture (V/V = 4/4 mL). $Pd(PPh_3)_2Cl_2$ (cat.) and CuI (cat.) were added. The solution was stirred overnight at room temperature. Ethyl acetate was added. The organic layer was washed with a solution of saturated ammonium chloride, water and brine. After drying on anhydrous Na_2SO_4, the solution was filtered, and solvents were removed under reduced pressure. (70 mg, 100 %). ^{1}H NMR (500 MHz, $CDCl_3$) : δ 7.73 (s, 2H), 7.67 (s, 2H), 7.38 (d, J = 8.6 Hz, 4H), 6.56 (d, J = 7.6 Hz, 4H), 3.27 (t, J = 7.6 Hz, 8H), 1.57 (m, 8H), 1.30 (m, 24H), 0.89 (t, J = 6.4 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) : δ 149.0, 137.4, 135.6, 133.7, 129.2, 124.5, 123.9, 123.4, 111.4, 107.5, 101.0, 85.9, 81.5, 79.9, 51.3, 32.0, 27.4, 27.1, 23.0, 14.3. HRMS (ESI) m/z calcd. for $[(M+ 2H)/2]^{2+}$ 543.0961, found 543.0940. HRMS (MALDI) m/z calcd. for $[M]^+$1084.1762, found 1084.1786 Elemental analysis calcd for $C_{56}H_{64}N_2Br_4$: C, 62.01; H, 5.95 ; N, 2.58. Found: C, 62.37; H, 5.99; N, 2.58.

UV-vis, λ_{max}(nm) [ε(M^{-1} cm^{-1})] = 440 [50 500]

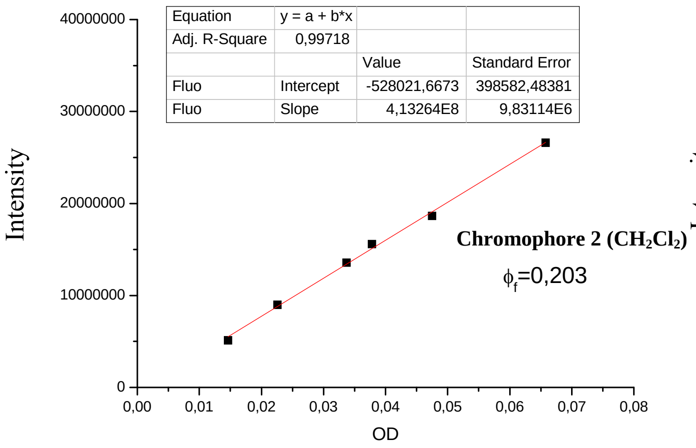
NMR spectra for chromophore 2



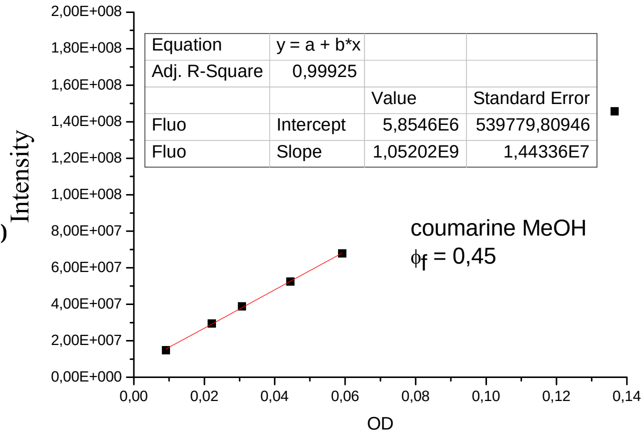



C_6H_{13}
N
C_6H_{13}
Br
Br
Br
Br
C_6H_{13}
N
C_6H_{13}
^{13}C NMR (CDCl$_3$)
500 MHz, 298K
14.3281
22.9595
27.0623
27.4439
31.9744
51.2606
77.0462
77.3002
77.5541
79.8855
81.4793
85.8619
101.0206
107.5206
111.4406
123.3613
123.4913
124.5116
129.2160
133.6629
135.5925
137.3977
148.9752
[ppm]
20
40
60
80
100
120
140
160
[rel]
10
8
6
4
2
0

Fluorescence quantum efficiency: plot of luminescence signal of chromophore 2 vs coumarine

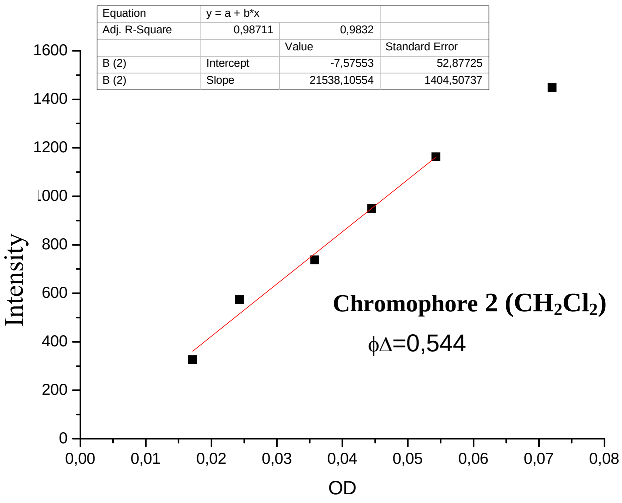


Equation	y = a + b*x		
Adj. R-Square	0,99718		
		Value	Standard Error
Fluo	Intercept	-528021,6673	398582,48381
Fluo	Slope	4,13264E8	9,83114E6

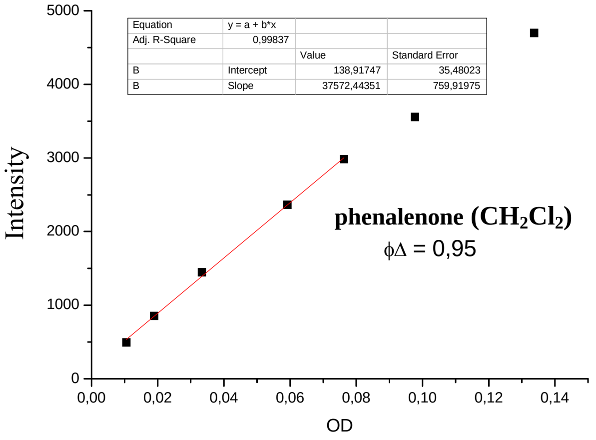


Equation	y = a + b*x		
Adj. R-Square	0,99925		
		Value	Standard Error
Fluo	Intercept	5,8546E6	539779,80946
Fluo	Slope	1,05202E9	1,44336E7

Singlet oxygen generation quantum efficiency: plot of singlet oxygen phosphorescence signal for chromophore 2 vs phenalenone



Equation	y = a + b*x		
Adj. R-Square	0,98711	0,9832	
		Value	Standard Error
B (2)	Intercept	-7,57553	52,87725
B (2)	Slope	21538,10554	1404,50737



Equation	y = a + b*x		
Adj. R-Square	0,99837		
		Value	Standard Error
B	Intercept	138,91747	35,48023
B	Slope	37572,44351	759,91975