Supplementary Material (ESI) for Chemical Communications

A tetraalkylated pyrene building block for the synthesis of pyrene-fused azaacenes with enhanced solubility

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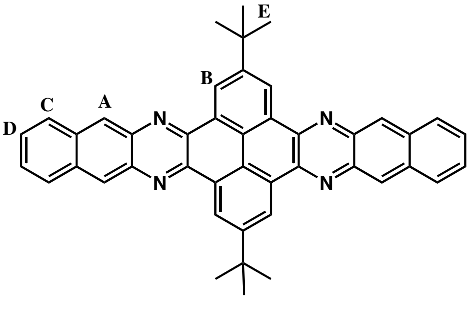
Synthesis and Characterisation

Commercial chemicals and solvents were used as received. Petrol ether refers to the fraction that distills between 40-60 °C. Anhydrous solvents were dried using a *MB SPS* Solvent Purification System. In the case of dry THF the first and second column is charged with molecular sieves (2Å) type II.

NMR spectra were recorded on a on a Varian Mercury 300 (300 MHz) and on a Bruker Avance DRX 500 (500MHz). Chemical shifts are reported in ppm using the solvent residual signal as an internal reference. Coupling costants (*J*) are given in Hz.
Mass Spectroscopy: Electrospray Ionization (ESI) and Atmosphere Pressure Chemical Ionization (APCI) were performed on a Thermo LCQ Advantage while the Electron Impact (EI) was performed on a Thermo TSQ700, at the Organische Chemie MS service (Universität Freiburg).
UV-Vis-NIR and **Emission** spectra were recorded on a Perkin-Elmer *Lambda 950* spectrometer, and a *LS55* Perkin-Elmer Fluorescence spectrometer, respectively.
Cyclic Voltammetry studies were carried out on a Princeton Applied Research *Parstat 2273* in a 3-electrode single compartment cell with Pt disk (∅=0.5 mm) working electrode, a platinum wire counter electrode and a silver wire reference electrode. The cell and the electrodes are custom-made.
Molecular models were performed with Spartan 08 (B3LYP/6-31G*).
Abbreviations: DCM (dichloromethane), THF (tetrahydrofuran), PE (Petrol Ether 40-60ºC), TFA (trifluoroacetic acid).

2,13-di-tertbutyl-tetraazaoctacene (4)



2,3-Diaminonaphtalene (71 mg, 0.45 mmol) and di-tertbutyl-tetraketopyrene[1](**2**) (84 mg, 0.22 mmol) were placed in previously dried schlenk flask. Anhydrous pyridine (10 ml) were added under Ar and the whole mixture was degassed 3 times. The resulting dispersion was heated at 120 °C under Ar for 3 days.

After cooling, EtOH was added and the formed brownish-orange precipitate was collected by filtration using Millipore® membranes (FGTP 0.2 μm). The filtrate was washed with EtOH (300 ml), $CHCl_3$ (20 ml) and then dried under vacuum to give the title compound as an orange solid (45 mg , 32 %).

^{1}H NMR (200 MHz, TFA-d*1*): 9.97 (s, 4H,HA); 9.23 (s, 4H, HB); 8.31 (m, 4H, HC); 7.86 (m, 4H, HD); 1.72 (s, 18H, HE).

MS (ESI): 619.3 (M^+ + 1), $C_{44}H_{35}N_4$ requires 619.3.

UV-vis (TFA, nm): 308, 348, 362, 470, 500.

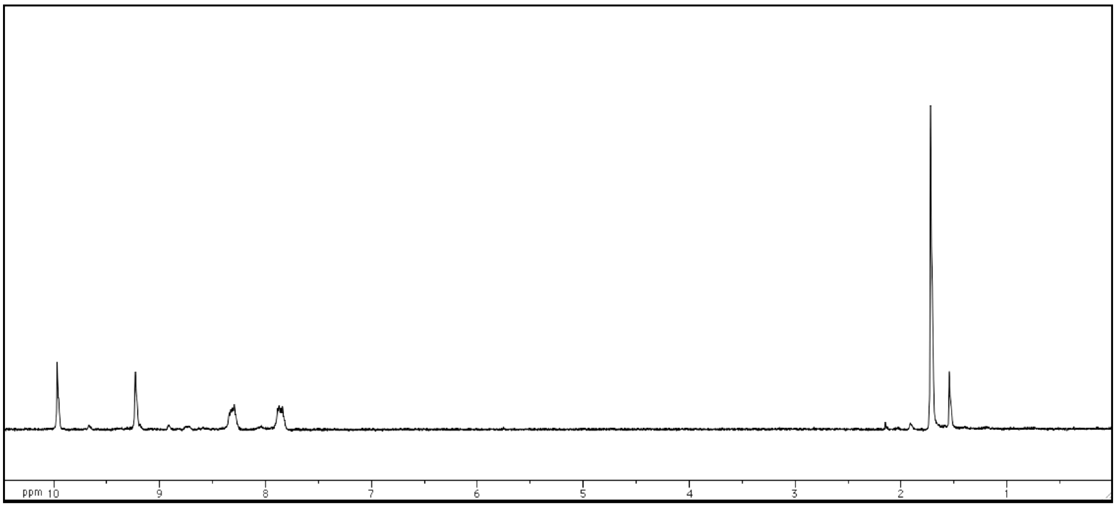


Figure S1: ^{1}H-NMR of **4** in TFA-*d*.

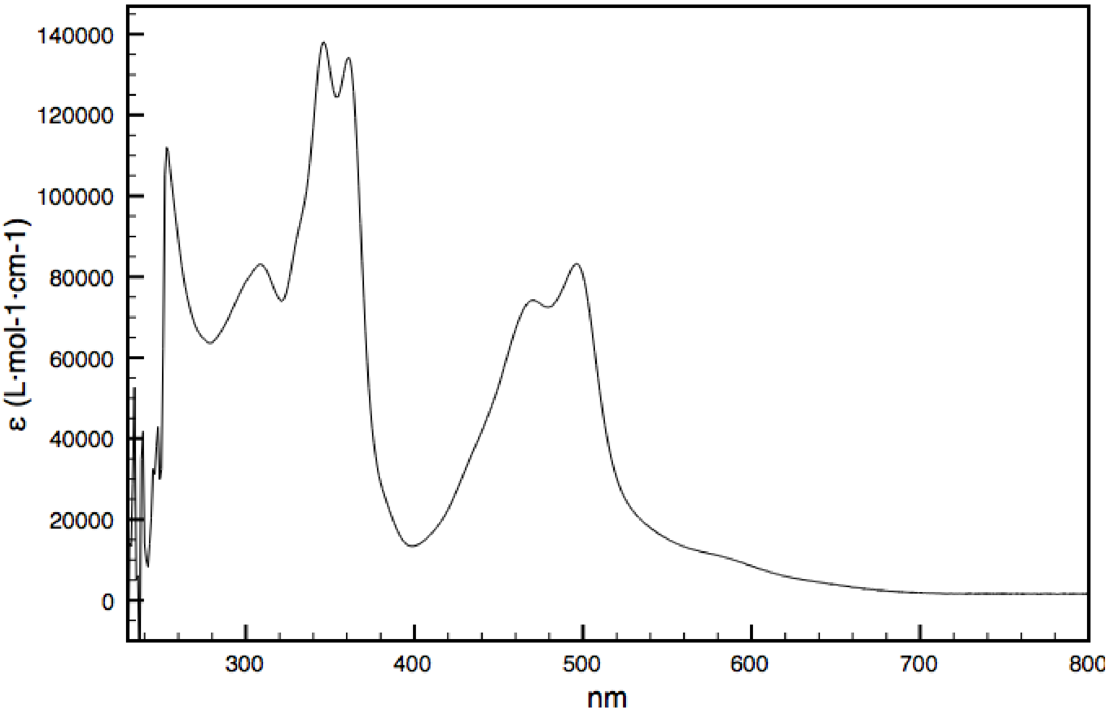
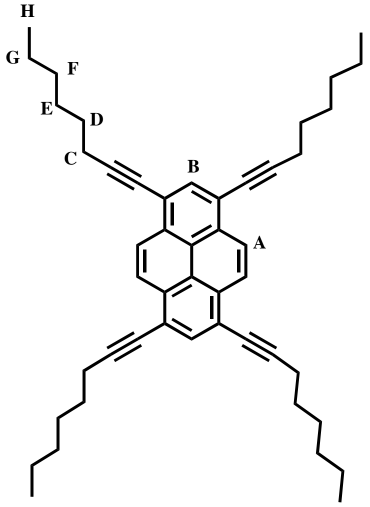


Figure S2: UV-vis of **4** in TFA.

1,3,6,8-tetraoctacyl-pyrene (7)



Tetrabromopyrene[2] (**5**) (1.015 g, 1.96 mmol) was added to a degassed solution of *i*-Pr_2NH (20 mL) and dry THF (20 mL). The solution was degassed. Subsequently CuI (21 mg, 0.11 mmol) and $[Pd(PPh_3)_2Cl_2]$ (71mg, 0.11 mmol) were added. The solution was degassed once again. 1-octyne (2 mL, 13.5 mmol) was added, the solution was once again degassed and heated at 80 °C under Ar overnight. The resulting mixture was filtered over celite and washed with 200 mL of CH_2Cl_2. Removal of the solvent under vacuum and purification of the crude by column chromatography (petrol ether) yielded a bright yellow solid (885 mg, 71 %yield).

^1H NMR (500 MHz, $CDCl_3$): 8.54 (s, 4H, H_A); 8.14 (s, 2H, H_B); 2.63 (t, 8H, $J = 7.1$ Hz, H_C); 1.76 (m, 8H, H_D); 1.59 (m, 8H, H_E); 1.39 (m, 16H, H_F-H_G); 0.94 (m, 12H, H_H).

^{13}C NMR (125 MHz, $CDCl_3$): 133.7, 131.5, 126.45, 124.5, 119.4, 97.1, 79.1, 31.5, 28.9, 28.8, 22.7, 20.0, 14.2.

MS (APCI): 635.4 ($M^+ + 1$), $C_{48}H_{59}$ requires 635.4.

UV-vis ($CHCl_3$, nm): 260, 310, 405, 420.

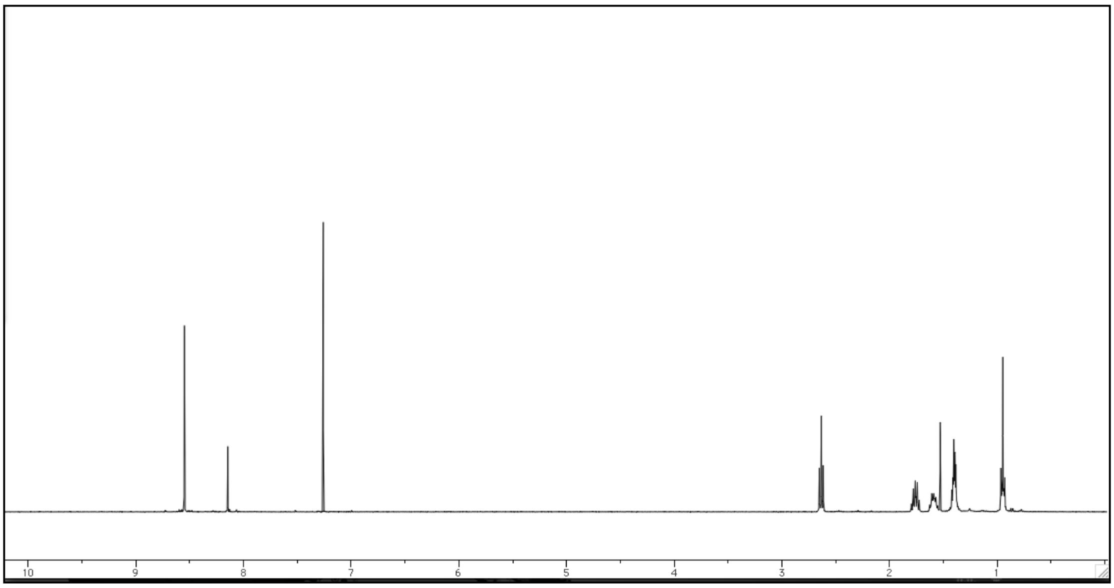


Figure S3: ^{1}H-NMR of **7** in $CDCl_3$.

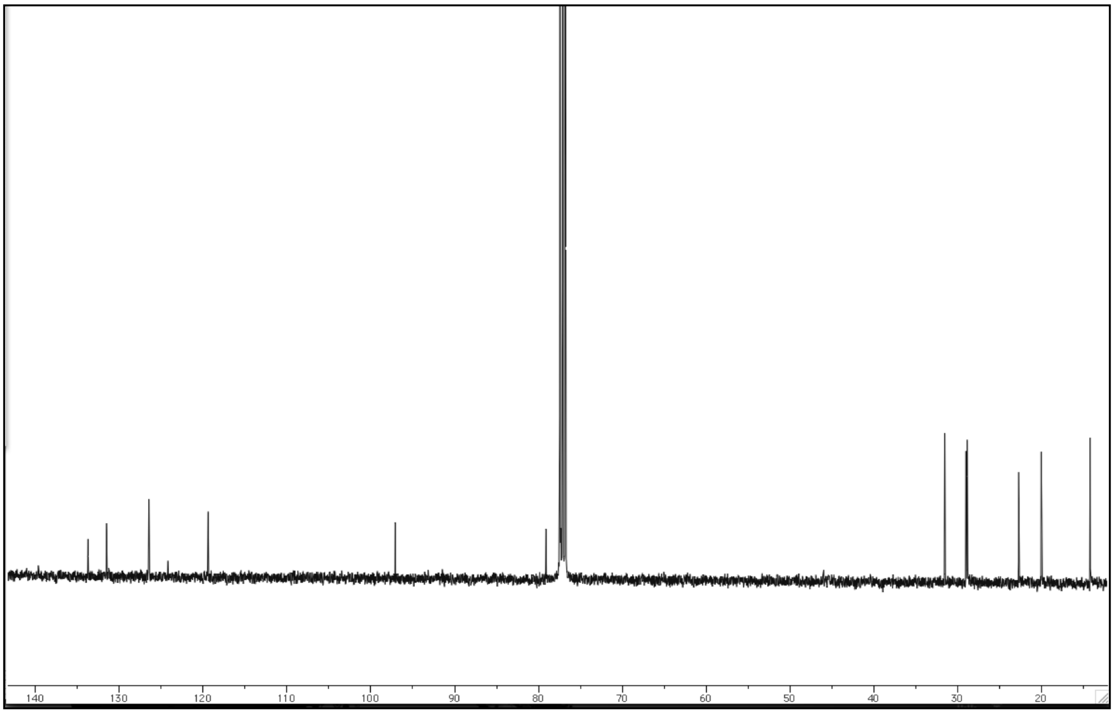


Figure S4: ^{13}C-NMR of **7** in $CDCl_3$.

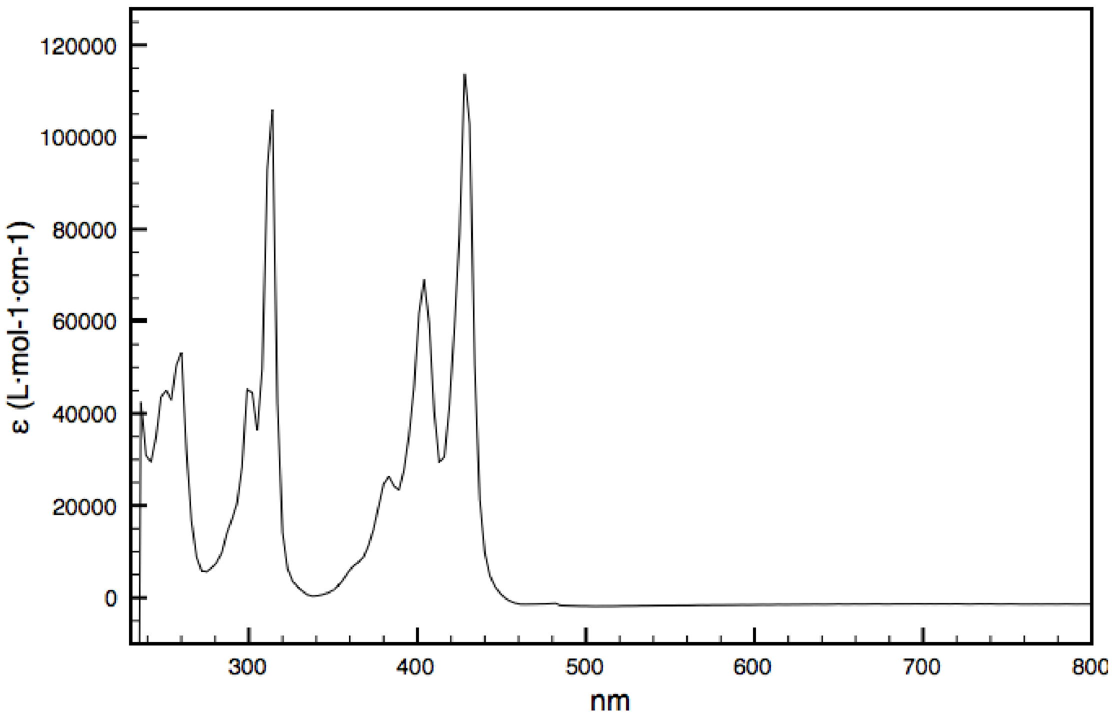
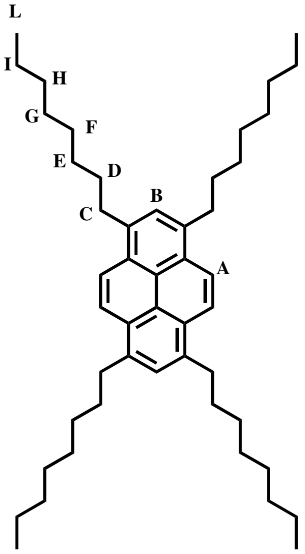


Figure S5: UV-vis of **7** in $CHCl_3$.

1,3,6,8-tetraoctyl-pyrene (8)



A solution of **7** (372 mg, 0.58 mmol) and Pd/C (52 mg, 10 %) in ethyl acetate was stirred at room temperature under H_2 atmosphere (balloon) for 16 h. The solution was filtered over celite for eliminating the Pd catalyst and the solvent was eliminated under vacum to yield 336 mg (89% yield) of a pale yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): 8.19 (s, 4H, H_A); 7.68 (s, 2H, H_B); 3.29 (t, 8H, $J = 7.8$ Hz, H_C); 1.84 (m, 8H, H_D); 1.48 (m, 8H, H_E); 1.29 (m, 24H, H_F-H_I); 0.89 (m, 12H, H_L).

^{13}C NMR (125 MHz, $CDCl_3$): 136.2, 128.8, 127.3, 126.5, 122.37, 33.8, 32.0, 30.1, 29.7, 29.4, 22.8, 14.2.

MS (APCI): 651.4 ($M^+ + 1$), $C_{48}H_{75}$ requires 651.6.

UV-vis ($CHCl_3$, nm): 251, 275, 287, 332, 347, 365.

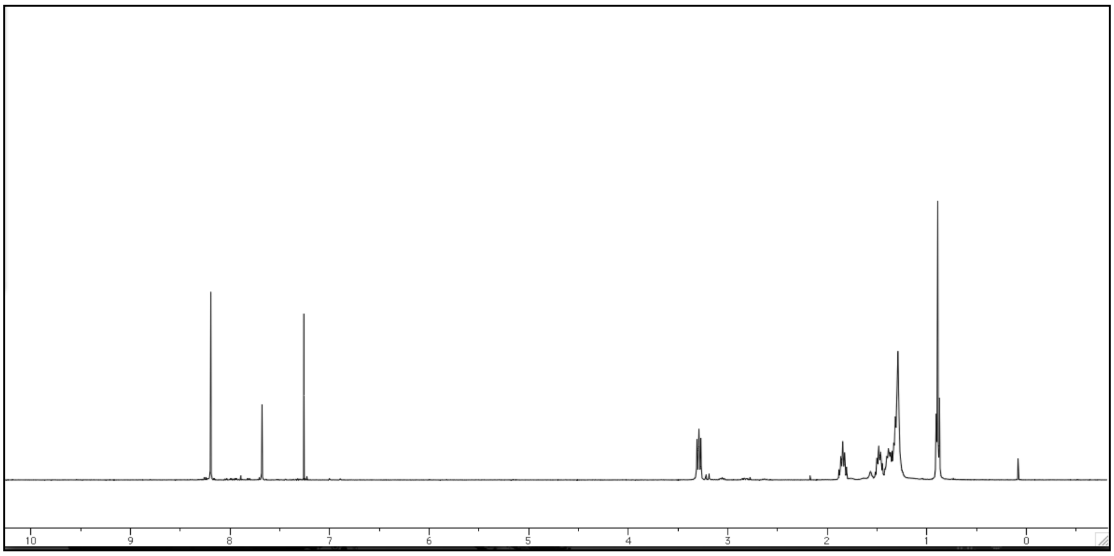


Figure S6: ^{1}H-NMR of **8** in $CDCl_3$.

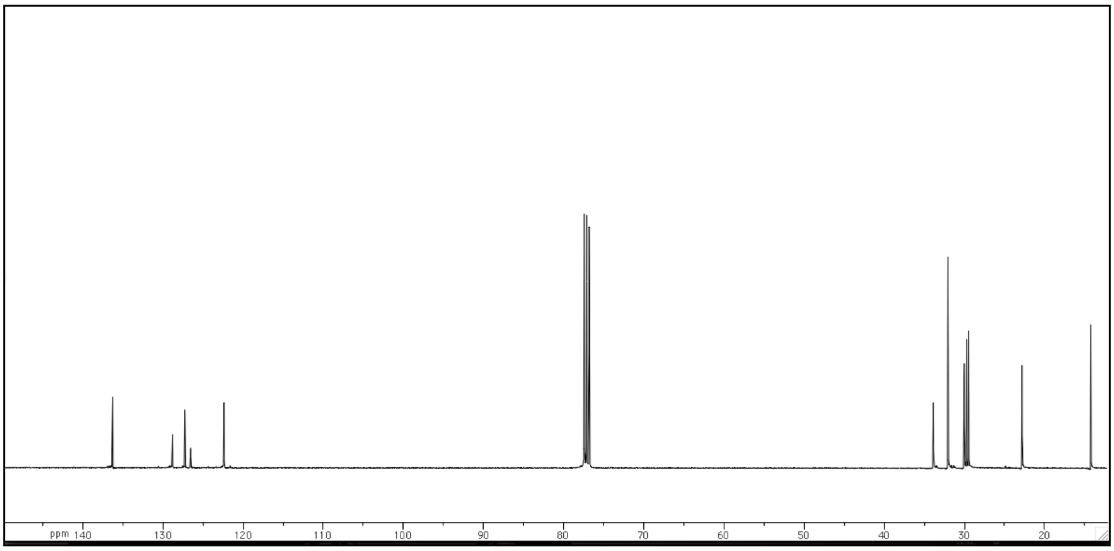


Figure S7: ^{13}C-NMR of **8** in $CDCl_3$.

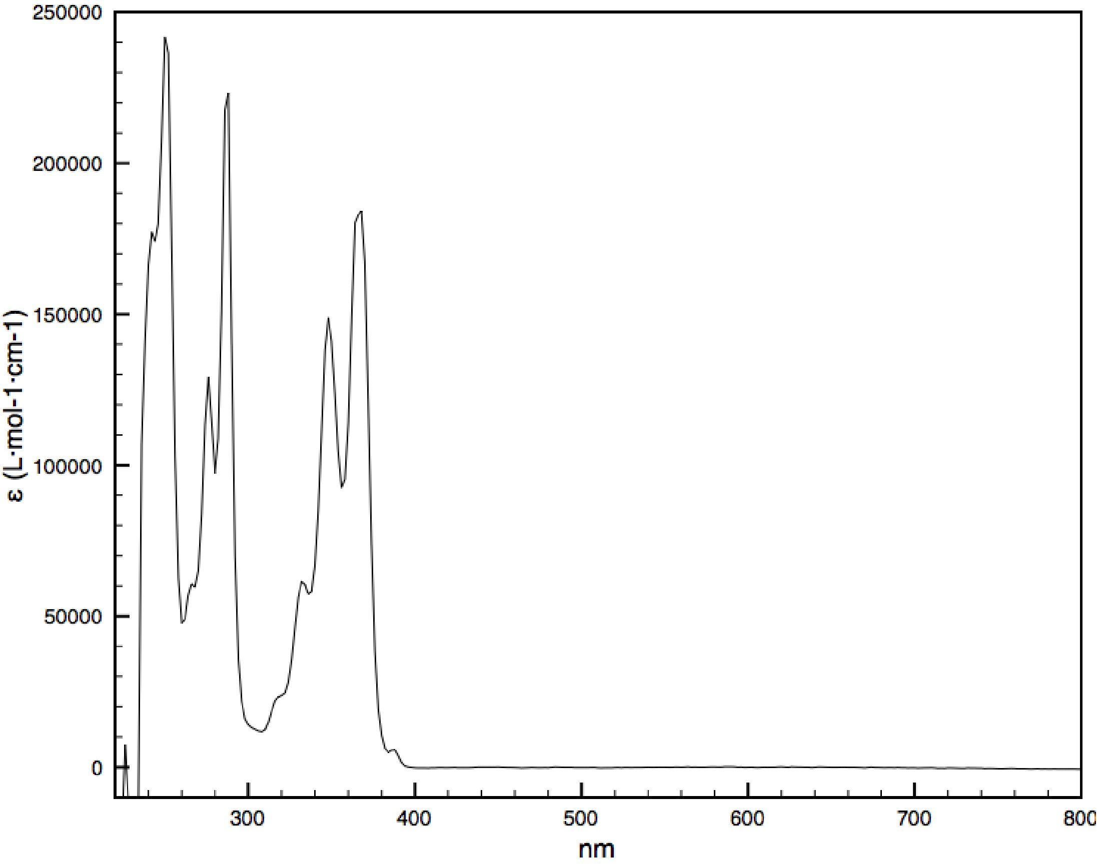
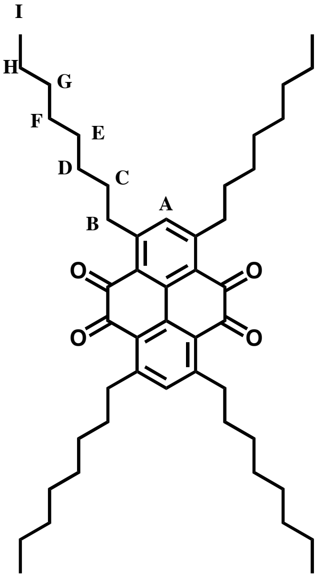


Figure S8: UV-vis of **8** in $CHCl_3$.

1,3,6,8-tetraoctyl-4,5,9,10-tetraketopyrene (9)



$NaIO_4$ (1.266 g, 5.9 mmol), water (40 mL) and $RuCl_3xH_2O$ (131 mg, 0.63 mmol) were successively added to a solution of **8** (482 mg, 0.74 mmol) in CH_2Cl_2 (30 mL) and CH_3CN (30 mL). The reaction mixture was stirred at 46 °C for 2 days. Water (150 mL) was added and the mixture was extracted with CH_2Cl_2 (3x100 mL). The organic phases were combined and washed with water (3x150 mL). The organic phase was then dried with dry $NaSO_4$, filtered and the solvent was eliminated under reduced pressure. Purification via column chromatography (petrol ether: CH_2Cl_2 = 8:2) yielded 105 mg (20 % yield) of **9**.

^1H NMR (500 MHz, $CDCl_3$): 7.20 (s, 2H, H_A); 3.01 (t, 8H, *J*=7.8 *Hz*, H_B); 1.62 (m, 8H, H_C); 1.44 (m, 8H, H_D); 1.27 (m, 4H, H_E-H_H); 0.88 (s, 12H, H_I).

^{13}C NMR (125 MHz, $CDCl_3$): 185.7, 154.62, 139.5, 136.7, 127.4, 35.8, 31.9, 29.9, 29.5, 29.3, 22.8, 14.2.

MS (APCI): 711.5 (M^+ + 1), $C_{48}H_{71}O_4$ requires 711.5.

UV-vis ($CHCl_3$, nm): 237, 270, 314.

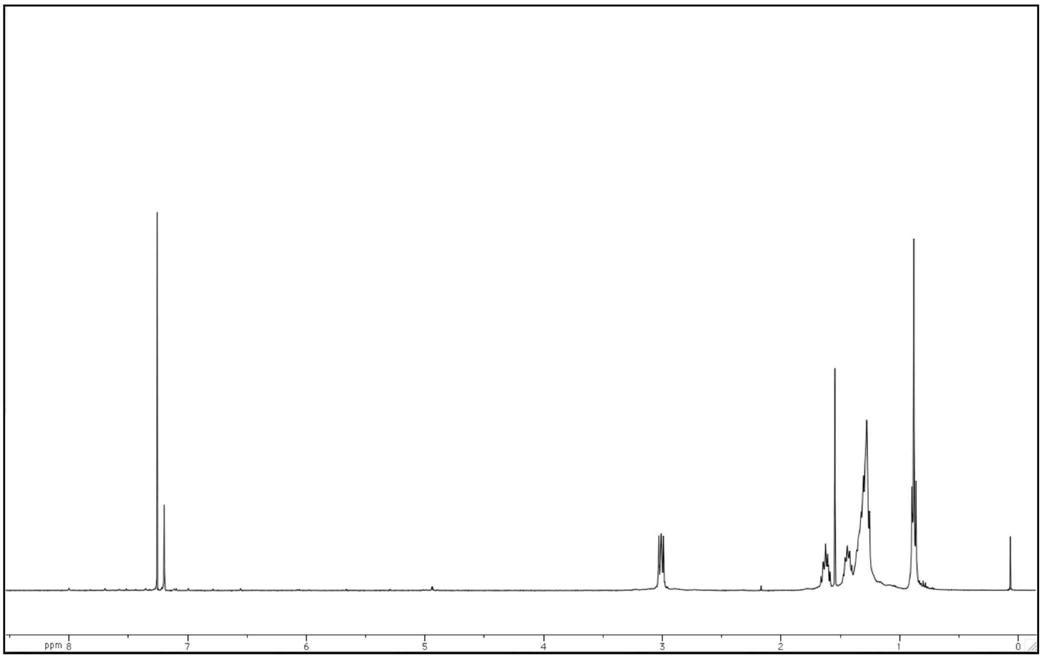


Figure S9: ^{1}H-NMR of **9** in $CDCl_3$.

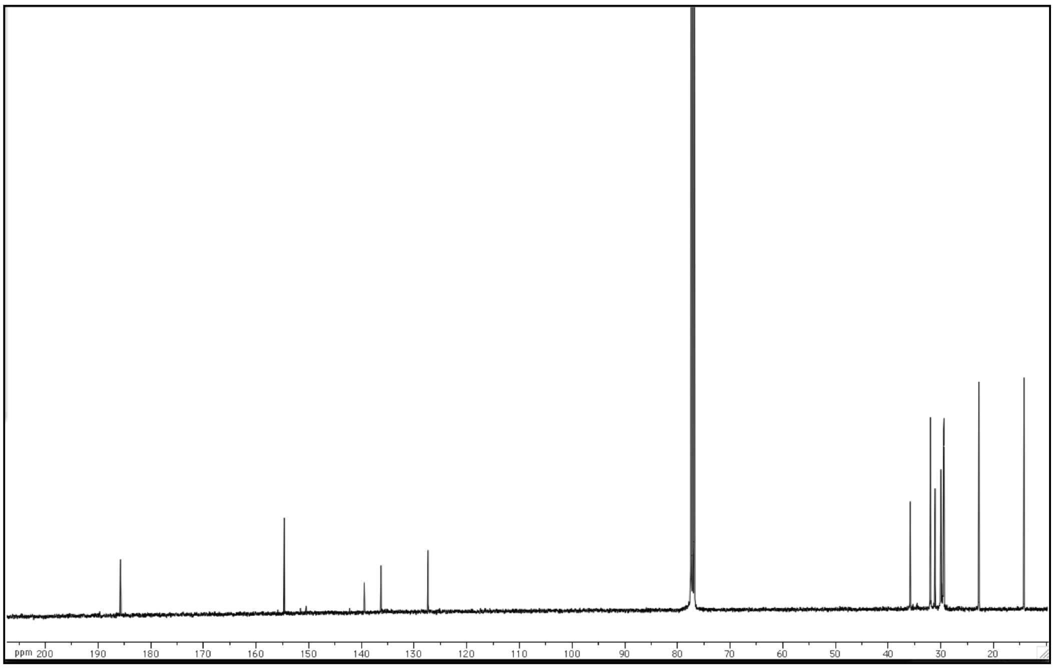


Figure S10: ^{13}C-NMR of **9** in $CDCl_3$

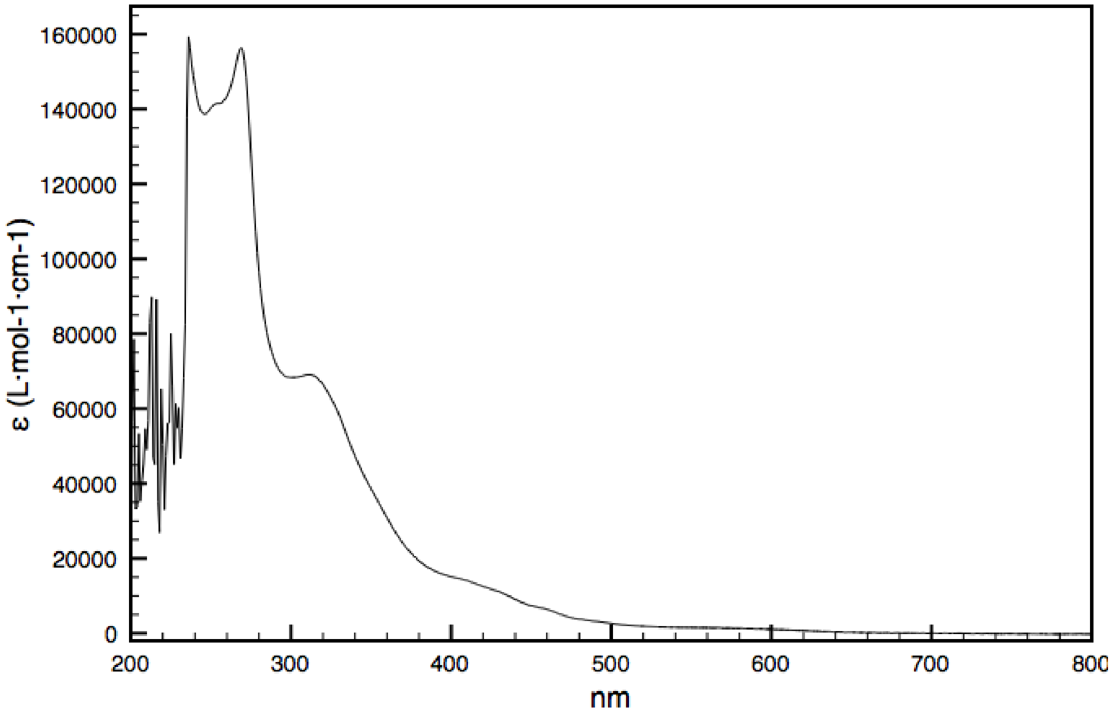
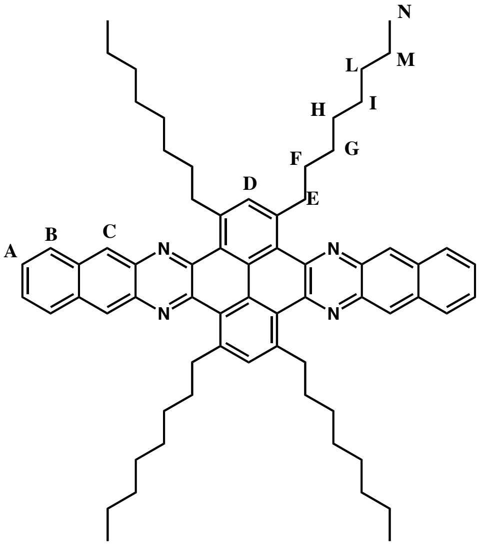


Figure S11: UV-vis of **9** in $CHCl_3$.

1,3,12,14-tetraoctyl-tetraazaoctacene (10)



2,3-Diaminonaphtalene (54 mg, 0.34 mmol) was added to a solution of **9** (110 mg, 0.15 mmol) in acetic acid (10 mL) under argon, in a previously flamed schlenk flask. The solution was stirred first for 12 hours at room temperature and subsequently 3 days at 120 °C in absence of light.

The resulting dark orange crude solution was dried under vacuum and purified by column chromatography (petrol ether: CH_2Cl_2= 85:15) to yield 24 mg (17% yield) of a bright yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$): 8.78 (s, 4H, H_C); 8.18 (m, 4H, H_B); 7.68 (s, 2H, *J* = 8 Hz, H_C); 7.59 (m, 4H, H_A); 3.82 (m, 8H, H_E); 3.08 (m, 8H, H_F); 1.72 (m, 8H, H_G); 1.50-1.25 (m, 32H, H_H, H_I, H_L, H_M); 0.92 (s, 12H, H_N).

^{13}C NMR (125 MHz, $CDCl_3$): 146.5, 145.6, 137.4, 136.4, 133.8, 133.0, 128.5, 126.9, 126.3, 125.8, 37.9, 32.1, 30.6, 29.8, 29.7, 22.8, 14.3.

MS (ESI): 955.6 (M^+ + 1), $C_{68}H_{82}N_4$ requires 955.6.

UV-Vis ($CHCl_3$, nm): 238, 255, 280, 323, 335, 434, 462.

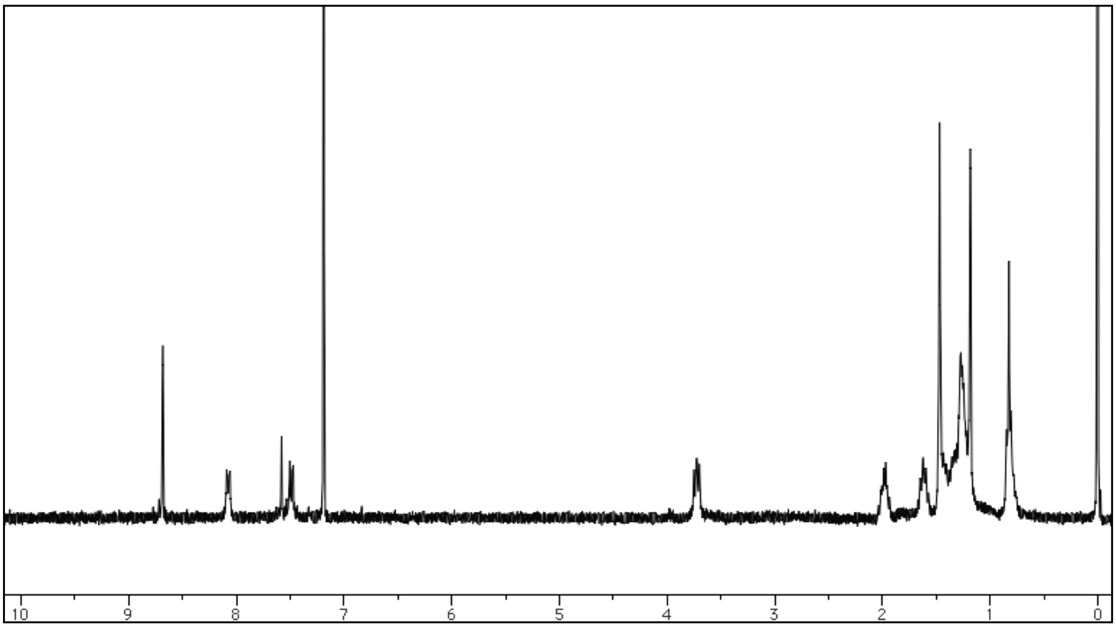
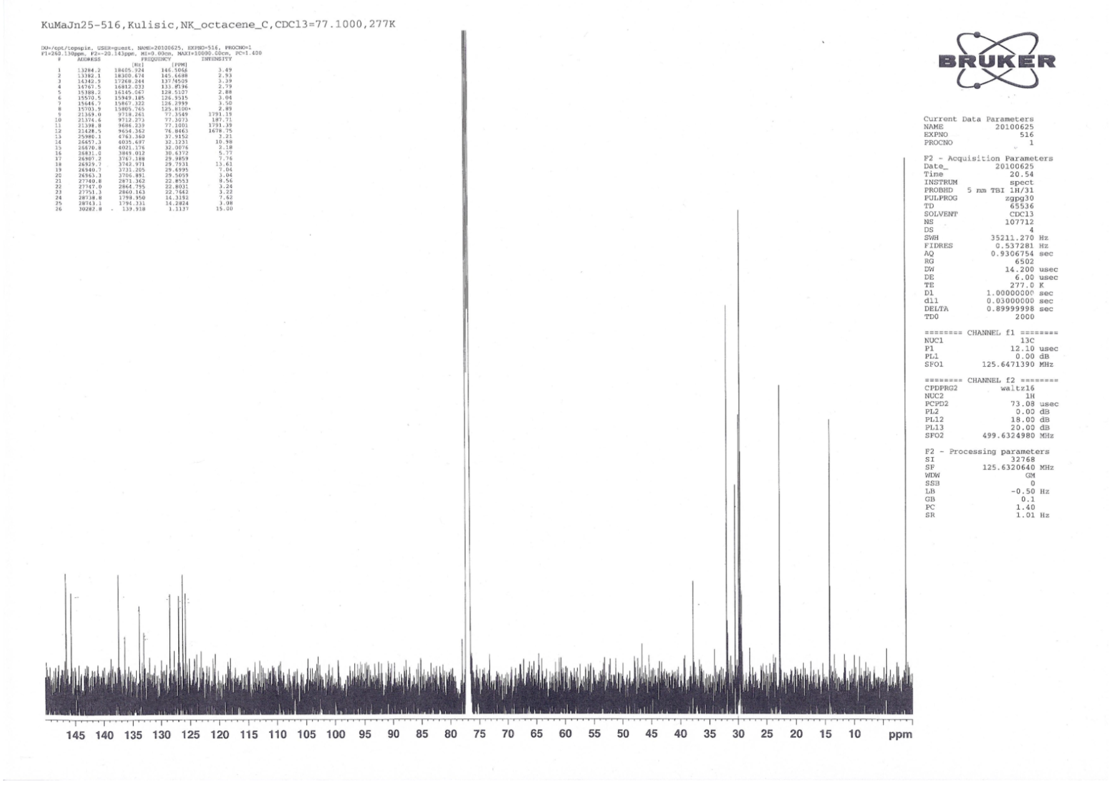


Figure S12: ^{1}H-NMR of **10** in CDCl$_3$.



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3	14342.9	17268.244	137.4509	3.39
4	14767.5	16812.033	133.8196	2.79
5	15388.2	16145.067	128.5107	2.88
6	15570.5	15949.185	126.9515	3.04
7	15646.7	15867.322	126.2999	3.50
8	15703.9	15805.765	125.8100	2.89
9	21369.0	9718.261	77.3549	1791.19
10	21374.6	9712.273	77.3073	187.71
11	21398.8	9686.239	77.1001	1791.39
12	21428.5	9654.362	76.8463	1678.75
13	25980.1	4763.360	37.9152	3.21
14	26657.3	4035.697	32.1231	10.98
15	26670.8	4021.176	32.0076	2.18
16	26831.0	3849.012	30.6372	5.77
17	26907.2	3767.188	29.9859	7.76
18	26929.7	3742.971	29.7931	13.61
19	26940.7	3731.205	29.6995	7.04
20	26963.3	3706.891	29.5059	3.04
21	27740.8	2871.362	22.8553	8.56
22	27747.0	2864.795	22.8031	3.24
23	27751.3	2860.163	22.7662	3.22
24	28738.8	1798.950	14.3192	7.62
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Figure S13: ^{13}C-NMR of **10** in CDCl$_3$

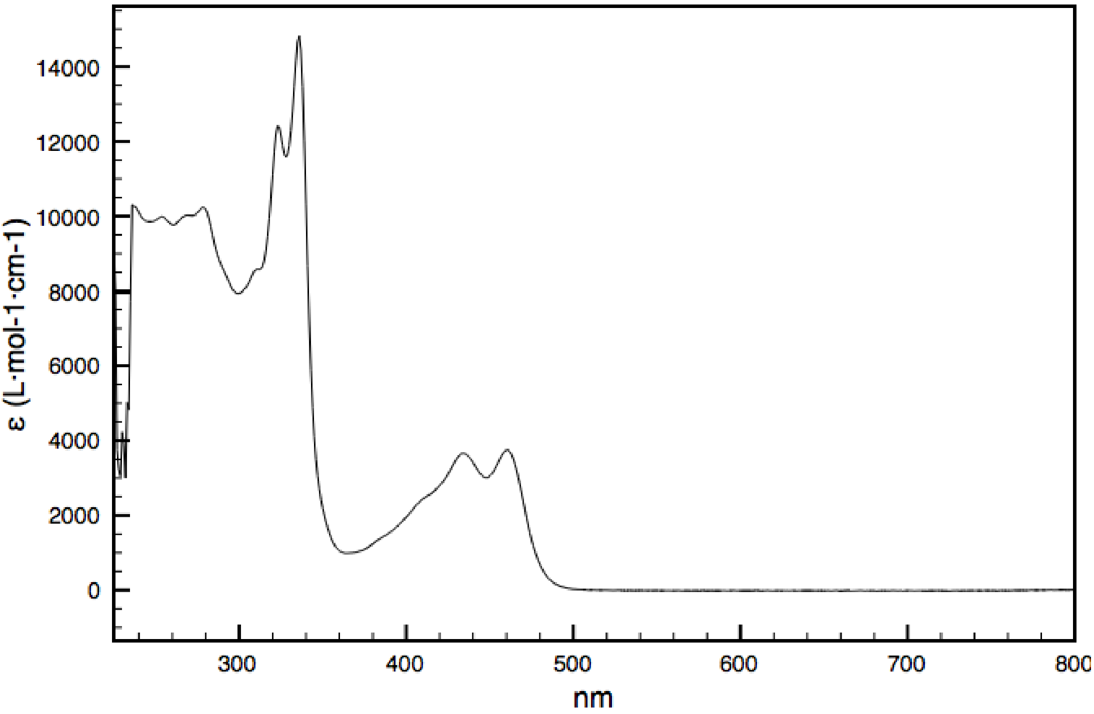

Figure S14: UV-vis of **10** in $CHCl_3$.

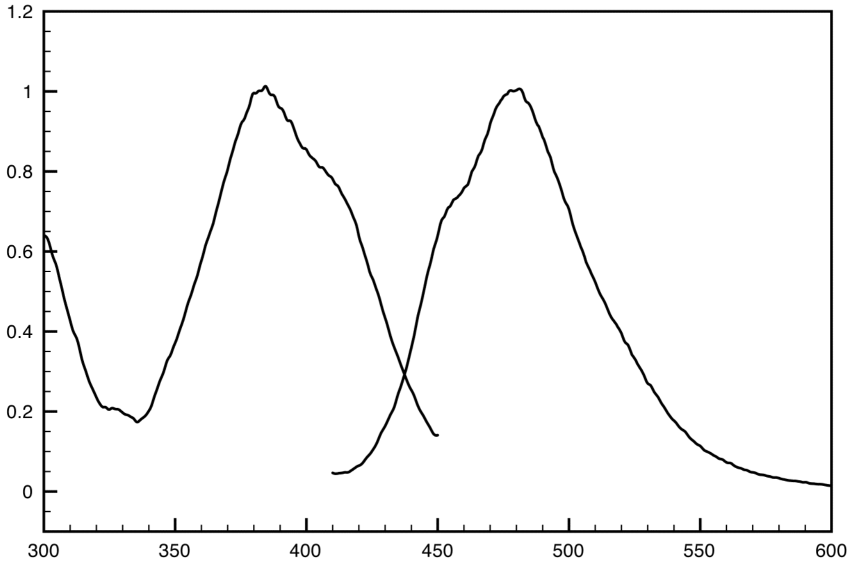

Figure S15. Emission and excitation spectra of **10** in $CHCl_3$.

References

1. J. Hu, D. Zhang and F. W. Harris, *J. Org. Chem.*, 2005, **70**, 707-708.

2. G. Venkataramana and S. Sankararaman, *Eur. J. Org. Chem.*, 2005, **2005**, 4162-4166.