Supporting Information

Fluorescent Probes based on Perylene-3,4,9,10-Tetracarboxylic Tetraesters

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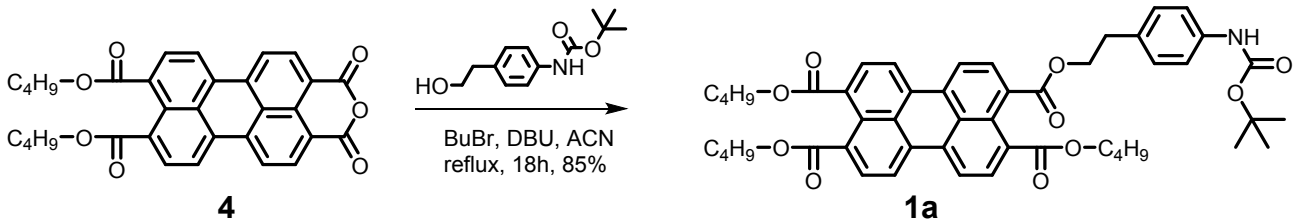
Index

Materials and Methods. All the reagents utilized were used as received from the manufacturer, unless otherwise stated. The DMF used in the synthesis was of anhydrous grade. 1,7-dibromoperylene tetrabutylester (**1**)[1] and *tert*-butyl-(4-hydroxyphenyl)carbamate and *tert*-butyl-(4-ethylhydroxyphenyl)carbamate [2] were prepared according to the previously reported procedures. The column chromatography was performed on silica gel 40–63 μm (230–400 mesh).

NMR spectra were recorded with a 400 MHz pulsed Fourier transform NMR spectrometer in $CDCl_3$ at room temperature. The chemical shifts are quoted relative to $CDCl_3$ [δ = 7.26 ppm (^{1}H, singlet); 77.00 (^{13}C, triplet)]. δ Values are given in ppm and J values in Hz.

UV-VIS and fluorescence spectra were taken in ethanol (Merck Uvasol), using a Bio-Tek Uvikon XL and a SPEX Fluorolog 3 spectrophotometer, respectively. Probe solubilities in ethanol were determined by adding an excess of probe to 5 mL ethanol, leaving the solution in a closed vial for 24 hours and measure the absorption of diluted samples. Probe concentrations for fluorescence measurements were typically 3-4 μmolar (A < 0.10) and excitation wavelength were chosen at the isosbestic points (471 and 470 nm for **1b** and **3**, respectively). Fluorescence quantum yields were determined using perylene-3,4,9,10-tetracarboxylic acid tetra potassium salt in water (Φ_F= 1.0) as a reference.[3] Measurements were taken at 4 different wavelengths (425, 430, 435 and 440 nm), in order to correct for eventual calibration differences in the absorption and emission spectrophotometers, and corrected for the use of different solvents.[4] All samples were degassed by purging with argon for 5 minutes.

Synthesis of 3-(4-((tert-butoxycarbonyl)amino)phenethyl) 10,4,9-tributyl perylene-3,4,9,10-tetracarboxylate (1a):



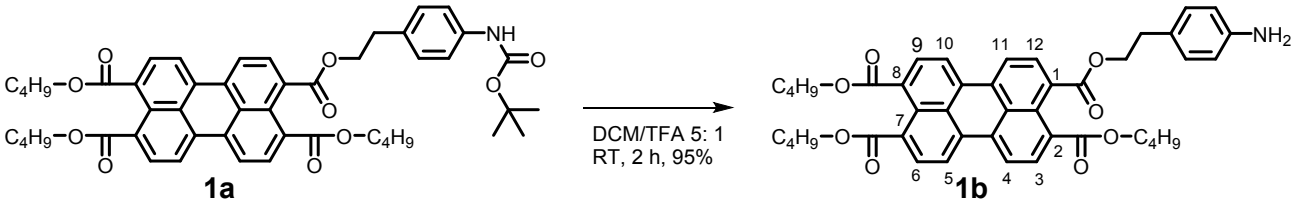
4 **1a**

In a 25 mL round-bottomed flask, weighed amounts of dibutylester perylene monoanhydride **4** (150 mg, 0.28 mmol), *tert*-butyl-(4-

ethylhydroxyphenyl)carbamate[5] 270 mg (1.15 mmol, 4eq), and DBU 170 mg (1.15 mmol, 4eq) were taken. Subsequently, anhydrous acetonitrile (5 mL) was added and the reaction mixture was stirred at RT for 1 h under argon atmosphere. Subsequently, bromobutane, 160 mg (1.17 mmol, 4eq) was added and the mixture was refluxed for 18 hours under argon atmosphere. After cooling the solvent was removed and the residue was dissolved in CH_2Cl_2 and extracted with water. The CH_2Cl_2 layer was isolated and dried with Na_2SO_4. After removing the solvent, ca 400 mg of an orange oil was isolated. The crude product was subjected to column chromatography (CH_2Cl_2-EtOAc 20:1) to afford the pure compound **1a** (200 mg, 0.24 mmol, 85%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 (m, J = 8.0 Hz, 4H), 8.02 (m, J = 8.0 Hz, 3H), 7.93 (d, J = 8.0 Hz, 1H), 7.32 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 6.44 (s, 1H), 4.50 (t, J = 7.2 Hz, 2H), 4.34 (m, 6H), 3.06, (t, J = 7.2 Hz, 2H), 1.79 (m, 6H), 1.51 (s, 9H), 1.48 (m, 6H), 1.01 (m, $J \sim$ 7.4 Hz 9H). MS (ESI-TOF): $[M+Na]^+$ Calculated for $C_{49}H_{53}NO_{10}$, 815.3669; found, 815.3713.

Synthesis of 3-(4-aminophenethyl) 10,4,9-tributyl perylene-3,4,9,10-tetracarboxylate (1b):



Boc-protected derivative **1a** (100 mg, 0.12 mmol) was dissolved in DCM (4 mL), TFA (1 mL) was then added, and the reaction mixture was stirred for 2 h at room temperature. The progress of the reaction was followed by TLC analysis. After the complete consumption of starting compound, DCM (25 mL) was added. The resultant solution was first washed with basic (K_2CO_3) aqueous solution, and then, with water. The organic layer was collected and evaporated. The crude product was subjected to column chromatography, using CH_2Cl_2, to afford the pure compound **1b** (83 mg, 95%). UV ($CHCl_3$): λ_{max} (ε)= 472 nm (43000), 443 nm (35000), 263 nm (28000).

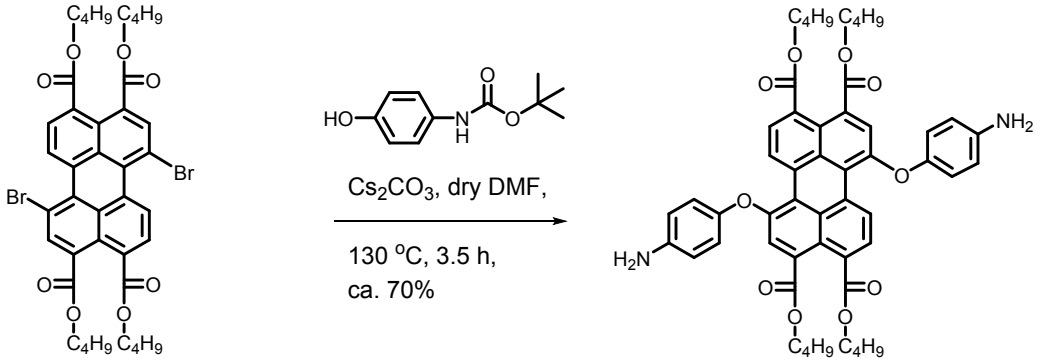
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (m, J = 8.0 Hz, 4H), 7.99 (m, J = 8.0 Hz, 3H), 7.92 (d, J = 8.0 Hz, 1H), 7.09 (d, J = 8.0 Hz, 2H), 6.66 (d, J = 8.0 Hz, 2H), 4.49 (t, J = 7.2 Hz, 2H), 4.33 (dt, J =

6.8 Hz, 6H), 3.01, (t, J = 7.4 Hz, 2H), 1.78 (m, J ~ 7 Hz, 6H), 1.50 (m, J ~ 7 Hz, 6H), 1.00 (dt, J = 7.4 Hz, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.57, 168.51, 168.37, 145.03, 132.51, 132.47, 130.23, 130.11, 130.08, 129.90, 129.76, 128.54, 128.35, 127.40, 66.10, 65.26, 34.20, 30.66, 19.27, 13.80 ppm.

MS (ESI-TOF): $[M+Na]^+$ Calculated for $C_{44}H_{45}NO_{10}$, 715.3145; found, 715.3164.

Synthesis of 1,7-di(4-aminophenoxy)perylene-3,4,9,10-tetracarboxy tetrabutylester (3):



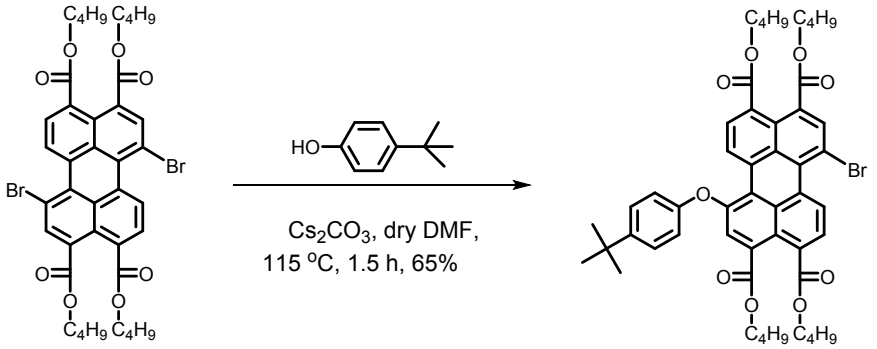
5 **3**

In a 25 mL round-bottomed flask, weighed amounts of 1,7-dibromoperylene tetrabutylester **5** (200 mg, 0.25 mmol), *tert*-butyl-(4-hydroxyphenyl)carbamate (206 mg, 0.99 mmol), and Cs_2CO_3 (483 mg, 1.48 mmol) were taken. Subsequently, anhydrous DMF (8 mL) was added. The reaction mixture was stirred at 130 °C for 3 h under argon atmosphere. After being cooled to room temperature, $CHCl_3$ (50 mL) was added to the reaction mixture and the resultant solution was washed with water several times. The organic layer was collected and evaporated. The crude product was subjected to column chromatography ($CHCl_3$;150:1 $CHCl_3$-EtOH) to afford the pure compound **4** (150 mg, 70%).[6] UV ($CHCl_3$): λ_{max} (ε)=482 nm (31000), 277 nm (39000).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.10 (d, J = 8.4 Hz, 2H), 7.99 (d, J = 8.4 Hz, 2H), 7.69 (s, 2H), 6.92 (d, J = 8.4 Hz, 4H), 6.71 (d, J = 8.4 Hz, 4H), 4.29 (t, J = 6.8 Hz, 4H), 4.23 (t, J = 6.8 Hz, 4H), 3.64 (s, 4H), 1.80–1.63 (m, 8H), 1.51−1.38 (m, 8H), 0.97 (t, J = 7.2 Hz, 6H), 0.93 ppm (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.61, 167.91, 153.29, 147.58, 143.24, 132.01, 131.34, 130.99, 129.11, 128.87, 127.07, 124.21, 123.15, 121.49, 120.70, 116.45, 65.30, 65.16, 30.62, 30.41, 19.23, 19.14, 13.78, 13.74 ppm.

MS (ESI-TOF): $[M+Na]^+$ Calculated for $C_{52}H_{54}N_2O_{10}$, 866.3778; found, 866.3840.

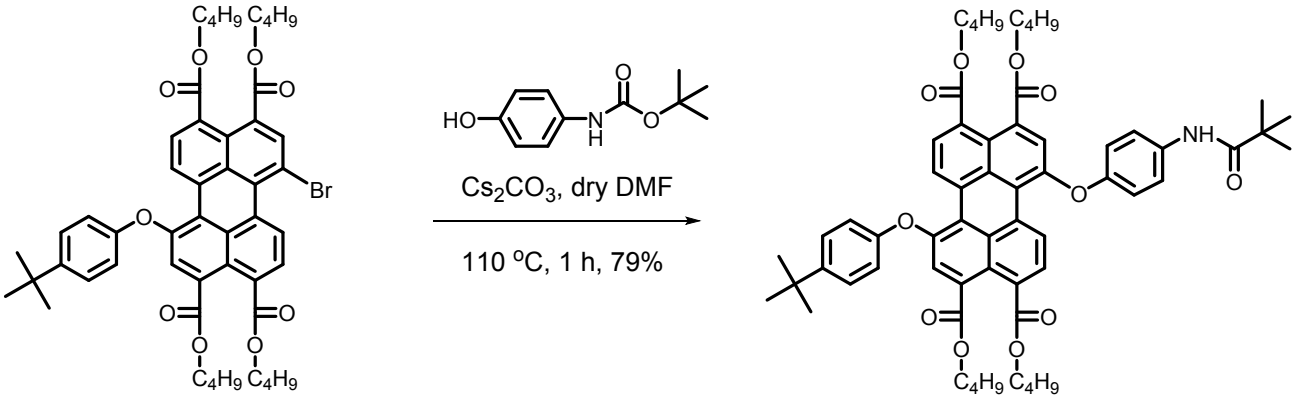
Synthesis of 1-bromo-7-(4-*tert*-butylphenoxy)perylene-3,4,9,10-tetracarboxy tetrabutylester (6):



5 **6**

A mixture of 1,7-dibromoperylene tetrabutylester **5** (500 mg, 0.62 mmol), 4-*tert*-butylphenol (112 mg, 0.74 mmol), and Cs_2CO_3 (606 mg, 1.86 mmol) was taken in anhydrous DMF (20 mL). The reaction mixture was stirred at 115 °C for 1.5 h under argon atmosphere. DCM (100 mL) was added to the reaction mixture after cooling it to room temperature. The resultant solution was washed several times with water containing little amount of HCl. The organic layer was collected and evaporated. The pure product (350 mg, 65%) was obtained by repeated column chromatography using DCM as eluent. Repeated column chromatography was required to fully separate the monosubstituted product **6** (R_f = 0.6) from the disubstituted product (R_f = 0.7) that was present in minor quantities in the reaction mixture. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.99 (d, J = 8.0 Hz, 1H), 8.92 (d, J = 8.0 Hz, 1H), 8.29 (s, 1H), 8.03 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.71 (s, 1H), 7.38 (d, J = 8.4 Hz, 2H), 7.00 (d, J = 8.4 Hz, 2H), 4.37–4.28 (m, 6H), 4.25 (t, J = 6.8 Hz, 2H), 1.84–1.65 (m, 8H), 1.55−1.32 (m, 8H), 1.33 (s, 9H), 1.05–0.95 (m, 9H), 0.91 ppm (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.33, 168.16, 167.61, 167.28, 153.05, 152.66, 147.31, 136.63, 132.62, 132.10, 131.84, 131.62, 131.57, 130.51, 130.46, 130.17, 130.03, 129.27, 127.81, 127.04, 126.79, 124.24, 123.99, 121.26, 118.48, 118.03, 65.64, 65.44, 65.34, 34.41, 31.43, 30.60, 30.57, 30.41, 19.22, 19.12, 13.78, 13.72 ppm.

Synthesis of 1-(Boc-protected 4-aminophenoxy)-7-(4-*tert*-butylphenoxy)perylene-3,4,9,10-tetracarboxy tetrabutylester (2a):

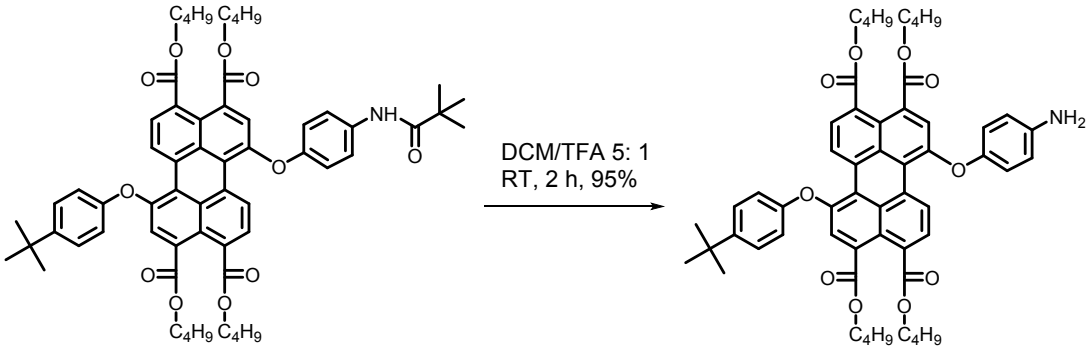


6 **2a**

A 25 mL flask was charged with mono-phenoxy derivative **6** (330 mg, 0.38 mmol), *tert*-butyl-(4-hydroxyphenyl)carbamate[7] (94 mg, 0.45 mmol), and Cs_2CO_3 (366 mg, 1.13 mmol). Subsequently, anhydrous DMF (10 mL) was added and the mixture was stirred at 110 °C for 1 h under argon atmosphere. DCM (100 mL) was added to the reaction mixture after cooling it to room temperature. The resultant solution was washed several times with water. The organic layer was collected and evaporated. The pure product (300 mg, 79%) was obtained by column chromatography in DCM.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.08 (d, J = 8.0 Hz, 1H), 9.04 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.73 (s, 1H), 7.69 (s, 1H), 7.40–7.35 (m, 4H), 7.05–6.96 (m, 4H), 6.48 (s, 1H), 4.32–4.18 (m, 8H), 1.80–1.60 (m, 8H), 1.51 (s, 9H), 1.50−1.33 (m, 8H), 1.32 (s, 9H), 0.99–0.86 ppm (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.49, 167.78, 167.72, 153.29, 152.82, 152.24, 152.18, 151.13, 147.01, 134.72, 131.95, 131.29, 131.24, 131.20, 131.14, 129.41, 129.13, 127.18, 127.13, 126.98, 124.66, 124.33, 123.98, 122.42, 122.34, 120.45, 119.51, 118.30, 65.42, 65.34, 65.23, 34.39, 31.44, 30.62, 30.44, 30.40, 28.32, 19.23, 19.14, 19.11, 13.77, 13.71 ppm.

Synthesis of 1-(4-aminophenoxy)-7-(4-*tert*-butylphenoxy)perylene-3,4,9,10-tetracarboxy tetrabutylester (2b):

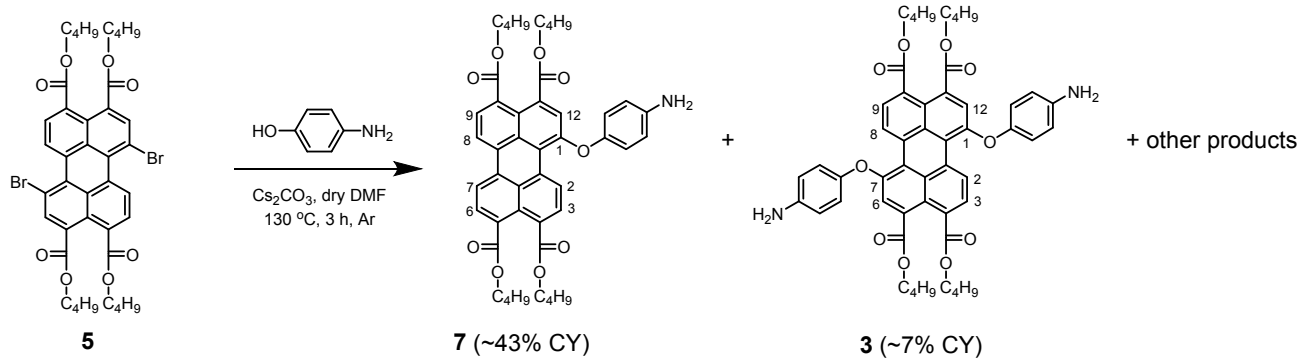


2a **2b**

Boc-protected derivative **2a** (200 mg, 0.20 mmol) was dissolved in DCM (6 mL), TFA (2 mL) was then added, and the reaction mixture was stirred for 2 h at room temperature. The progress of the reaction was followed by TLC analysis. After the complete consumption of starting compound, DCM (50 mL) was added. The resultant solution was first washed with basic (K_2CO_3) aqueous solution, and then, with water. The organic layer was collected and evaporated. The crude product was subjected to column chromatography, using $CHCl_3$, to afford the pure compound **2b** (172 mg, 95%). UV ($CHCl_3$): λ_{max} (ε)= 479 nm (29000), 272 nm (34000).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.12 (d, J = 8.0 Hz, 1H), 9.07 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.73 (s, 1H), 7.68 (s, 1H), 7.37 (d, J = 8.4 Hz, 2H), 7.00 (d, J = 8.2 Hz, 2H), 6.92 (d, J = 8.4 Hz, 2H), 6.71 (d, J = 8.2 Hz, 2H), 4.32–4.17 (m, 8H), 3.65 (s, 2H), 1.77–1.61 (m, 8H), 1.50−1.33 (m, 8H), 1.32 (s, 9H), 0.98–0.85 ppm (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.56, 167.85, 153.45, 153.37, 152.02, 147.47, 146.93, 143.36, 132.04, 131.95, 131.48, 131.14, 131.10, 129.36, 129.17, 128.83, 127.13, 127.09, 126.96, 124.72, 124.36, 124.18, 123.09, 122.63, 121.29, 120.76, 118.25, 116.45, 65.32, 65.19, 34.38, 31.44, 30.65, 30.42, 19.25, 19.15, 13.78, 13.73 ppm.

MS (ESI-TOF): $[M+Na]^+$ Calculated for $C_{56}H_{61}NO_{10}$, 907.4295; found, 907.4307.



5 **7** (~43% CY) **3** (~7% CY)

Scheme S1. Reaction of 1,7-dibromoperylene tetrabutylester 6 with 4-hydroxyaniline under standard substitution conditions.

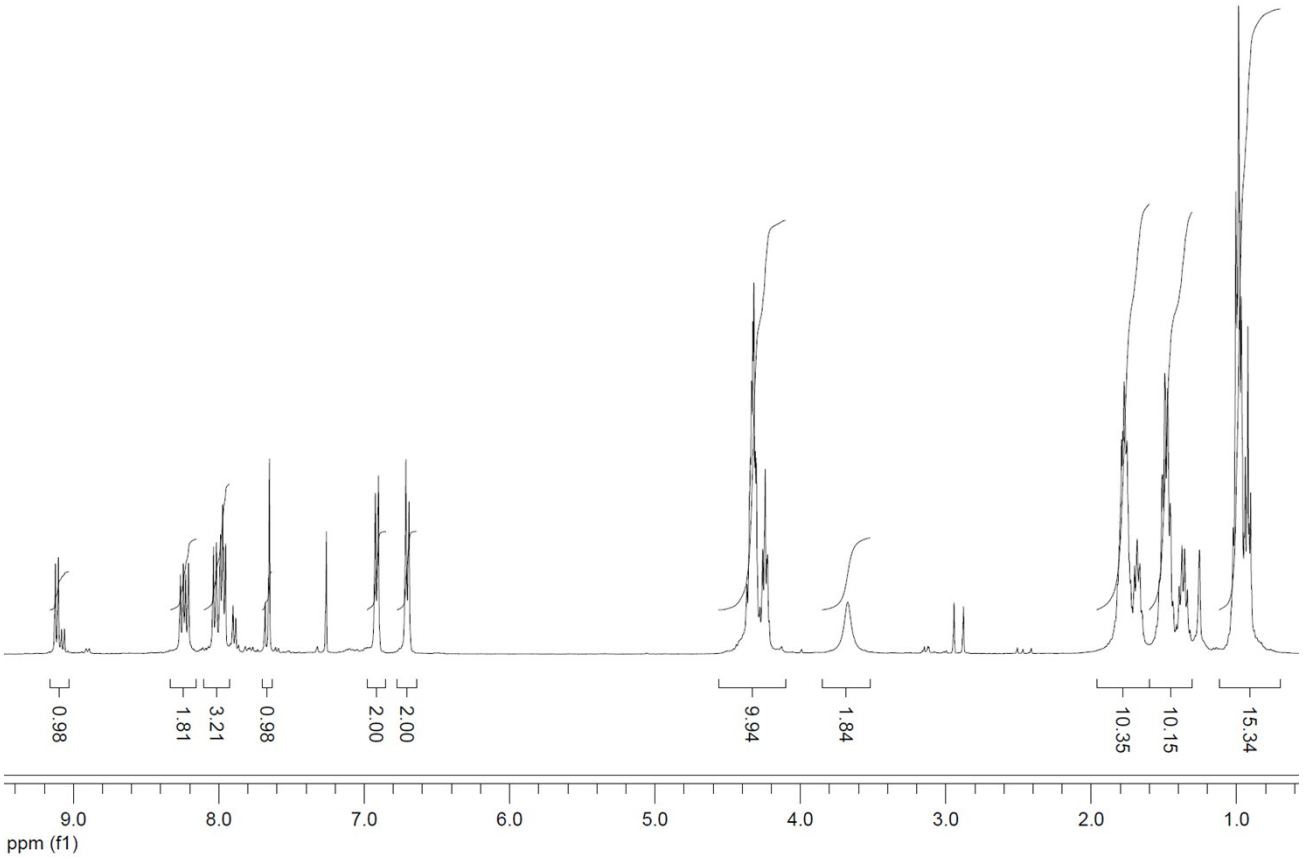


Figure S1. ^{1}H NMR of the product of the reaction of 1,7-dibromoperylene tetrabutylester 5 with 4-hydroxyaniline. This product was isolated after column chromatography.

The perylene resonances of compound **3** are clearly visible in the aromatic region: δ = 9.10 (d, J = 8.4 Hz, 2H), 7.99 (d, J = 8.4 Hz, 2H), 7.69 (s, 2H).

Much larger are the aromatic resonance of compound 7, a triple AB system with chemical shifts around 9.18 (1H), 8.22 (2H), 8.05 (3H) and a large singlet at 7.65 (1H).

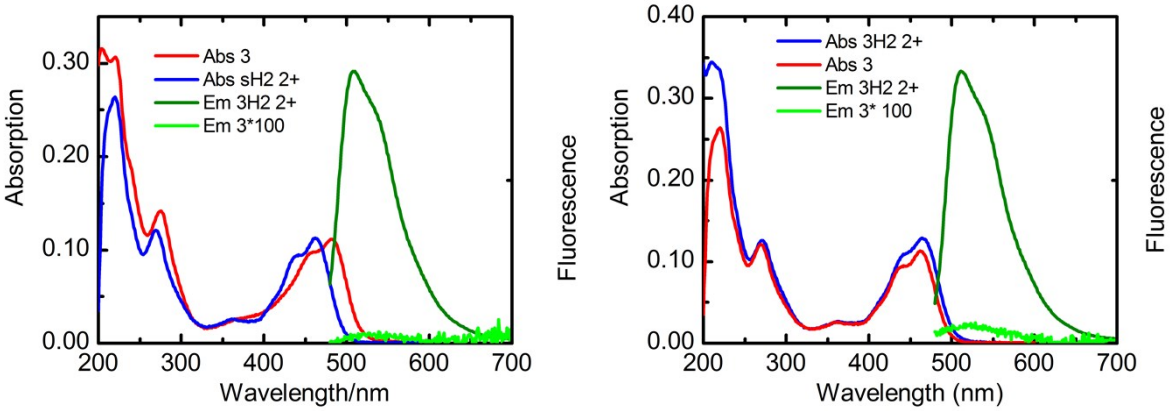


Figure S2. Absorption and emission spectra of **3** and $\mathbf{3H}_2^{2+}$ in ethanol (left) and etanol/water 1:1 (right), [**3**]= 3.2 umol/l in both cases. Compound $\mathbf{3H}_2^{2+}$ was formed by the addition of HCl. The fluorescence intensity of **3** was magnified by a factor 100 in both graphs.

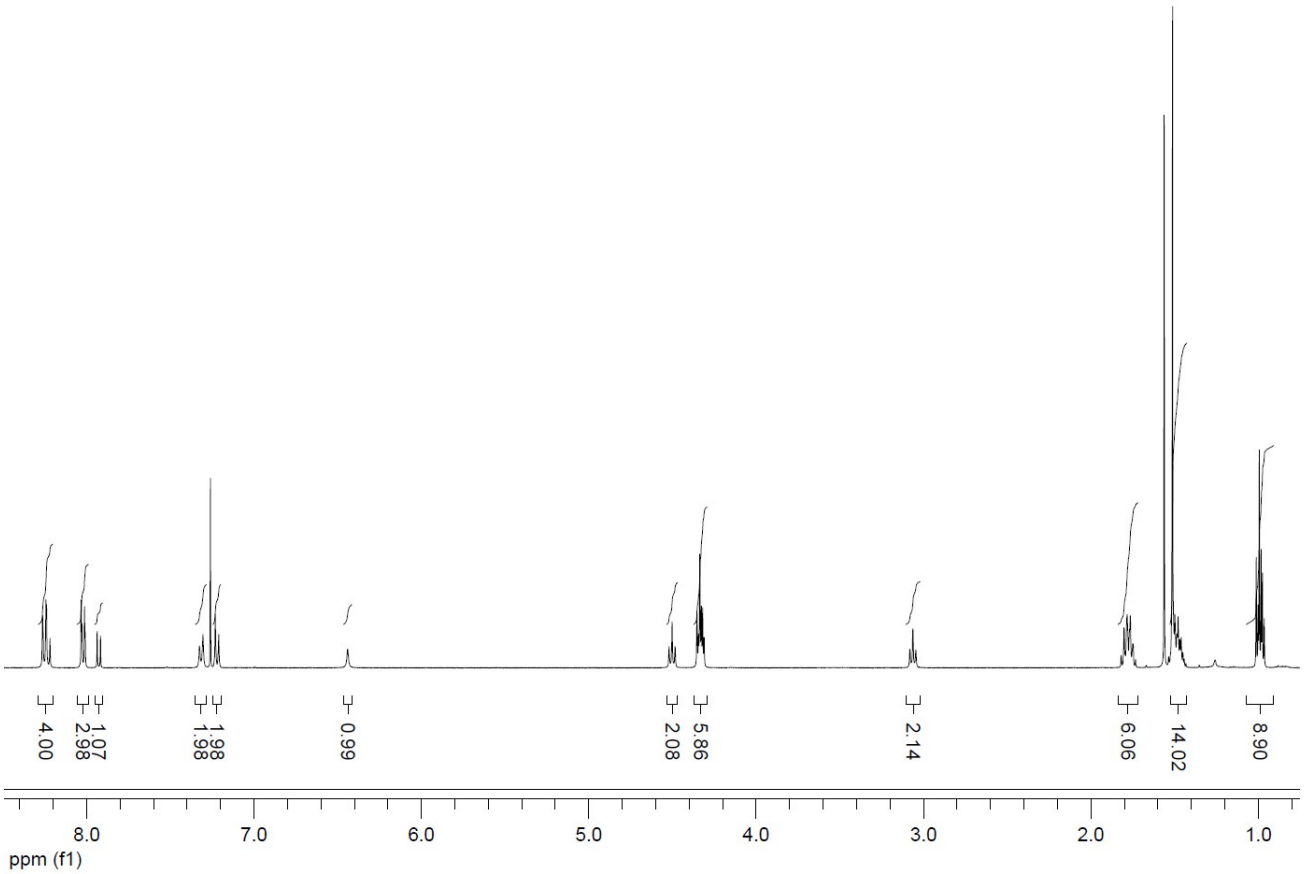


Figure S3. ^{1}H spectrum of 3-(4-((tert-butoxycarbonyl)amino)phenethyl) 10,4,9-tributyl perylene-3,4,9,10-tetracarboxylate (1a) in $CDCl_3$.

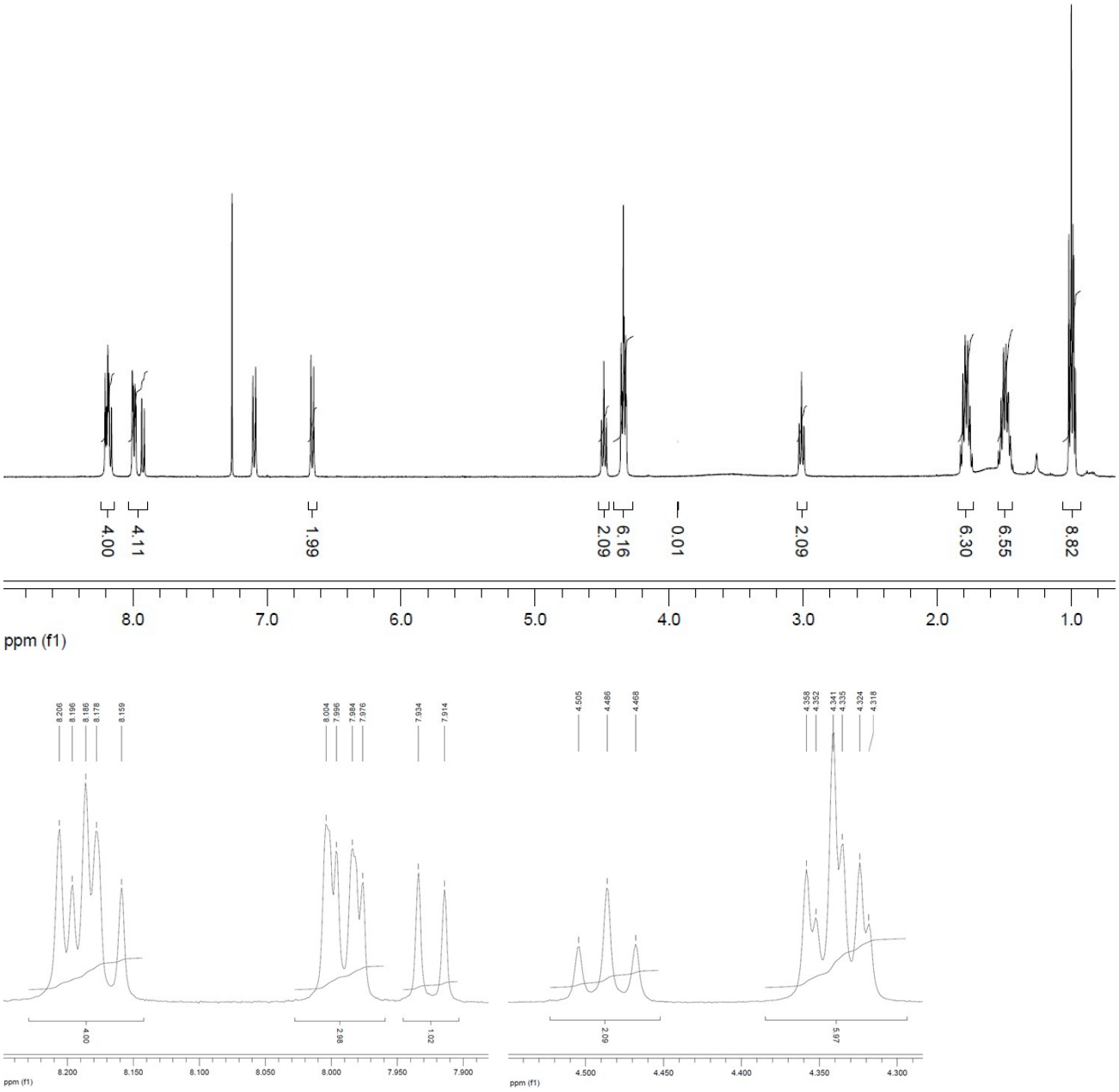


Figure S4. ^{1}H spectra of 3-(4-aminophenethyl) 10,4,9-tributyl perylene-3,4,9,10-tetracarboxylate (**1b**) in $CDCl_3$. The spectra below show the aromatic perylene protons (left) and the methylene ester protons (right).

The NMR spectra in Figure S4 indicate that the aromatic protons on the "right side" of compound **1b** (H_3,H_4 and H_{11},H_{12}) have different chemical shifts and form two distinguishable AB systems, whereas the aromatic proton on the "left side"(H_5,H_6 and H_9,H_{10}) have identical chemical shifts and form a single AB system. The same line of reasoning applies to the methylene ester protons on "both sides" of compound **1b**.

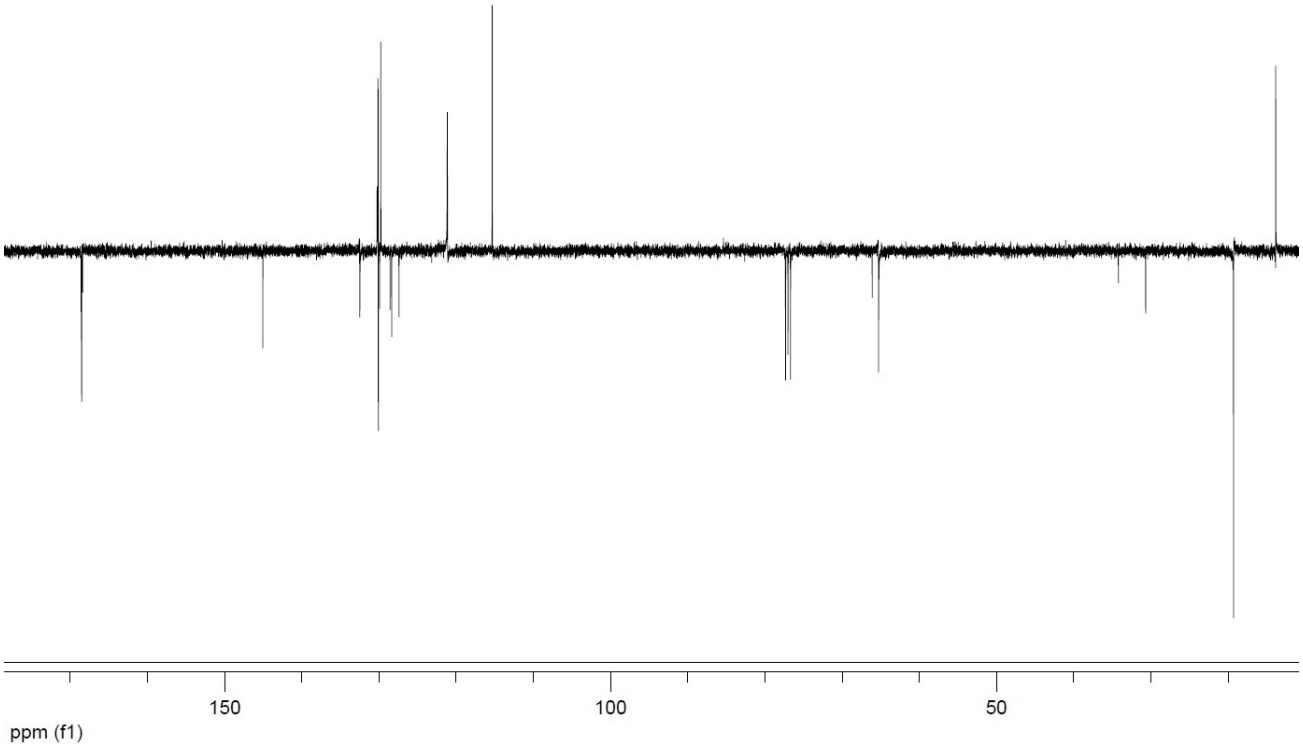


Figure S5. ^{13}C NMR spectrum of 3-(4-aminophenethyl) 10,4,9-tributyl perylene-3,4,9,10-tetracarboxylate (1b) in $CDCl_3$.

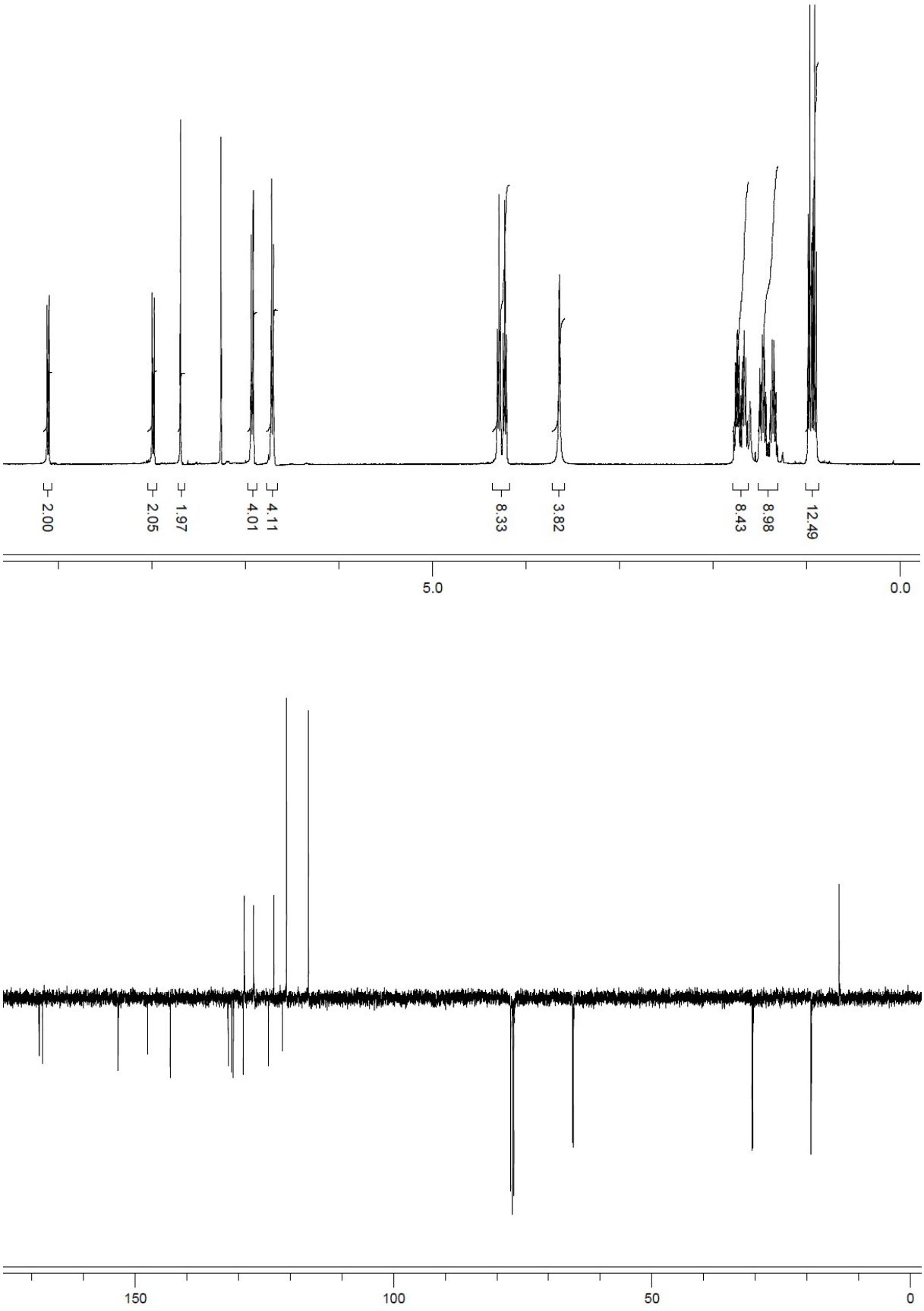


Figure S6. ^{1}H and ^{13}C NMR spectra of 1,7-di(4-aminophenoxy)perylene-3,4,9,10-tetracarboxy tetrabutylester (3) in $CDCl_3$.

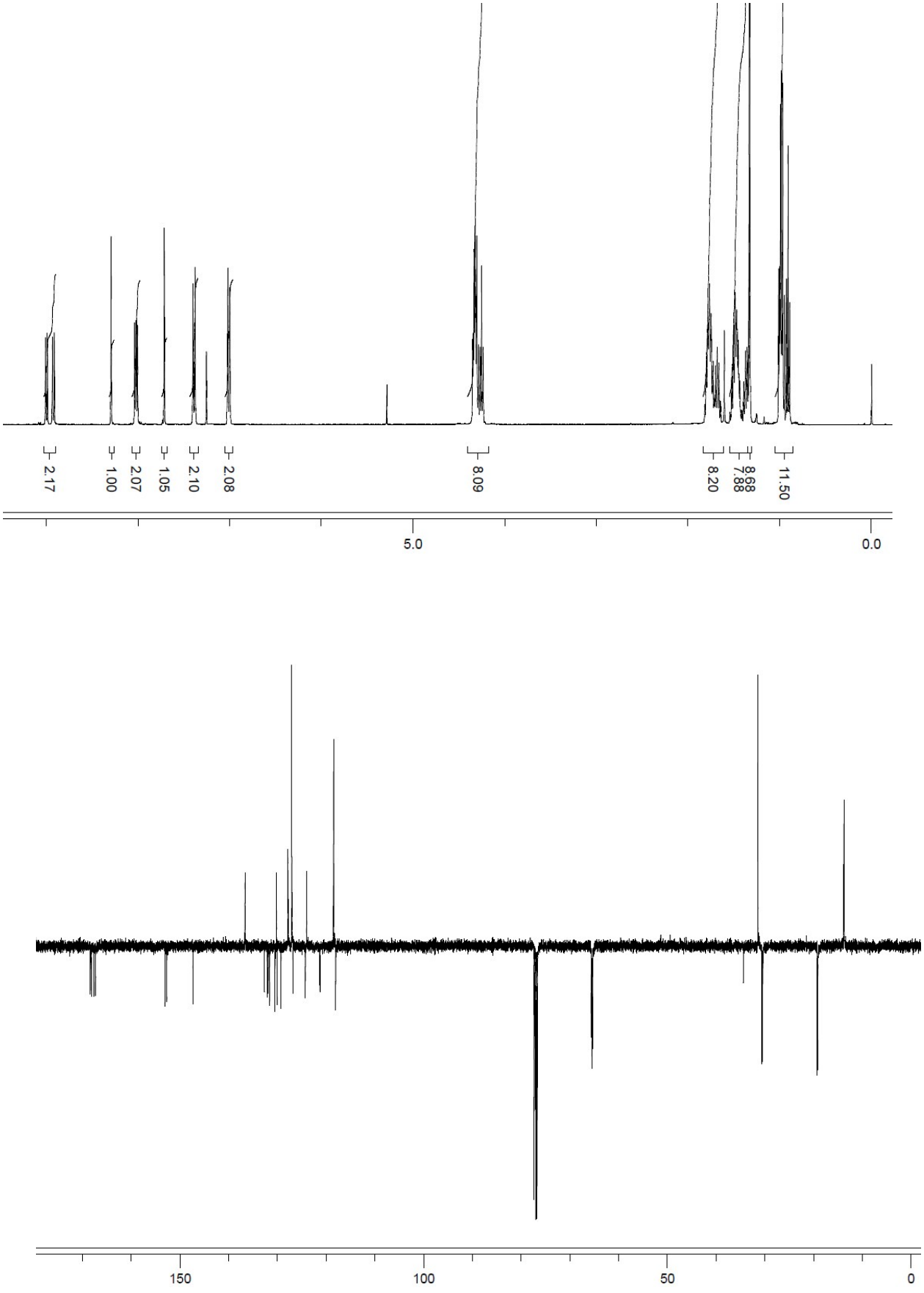


Figure S7. ^{1}H and ^{13}C NMR spectra of 1-bromo-7-(4-*tert*-butylphenoxy)perylene-3,4,9,10-tetracarboxy tetrabutylester (6) in $CDCl_3$.

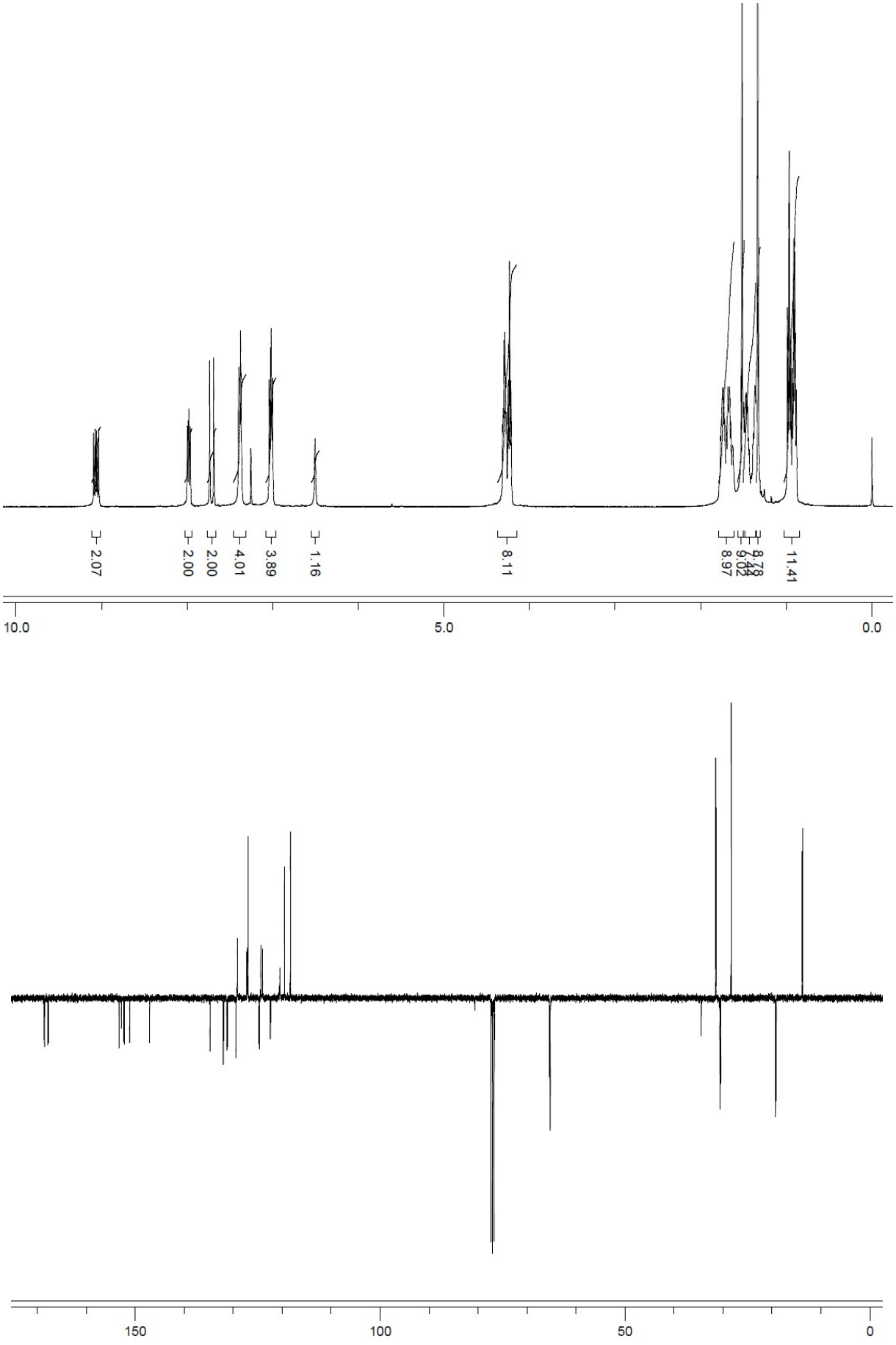


Figure S8. ^{1}H and ^{13}C NMR spectra of 1-(Boc-protected 4-aminophenoxy)-7-(4-*tert*-butylphenoxy)perylene-3,4,9,10-tetracarboxy tetrabutylester (2a) in $CDCl_3$.

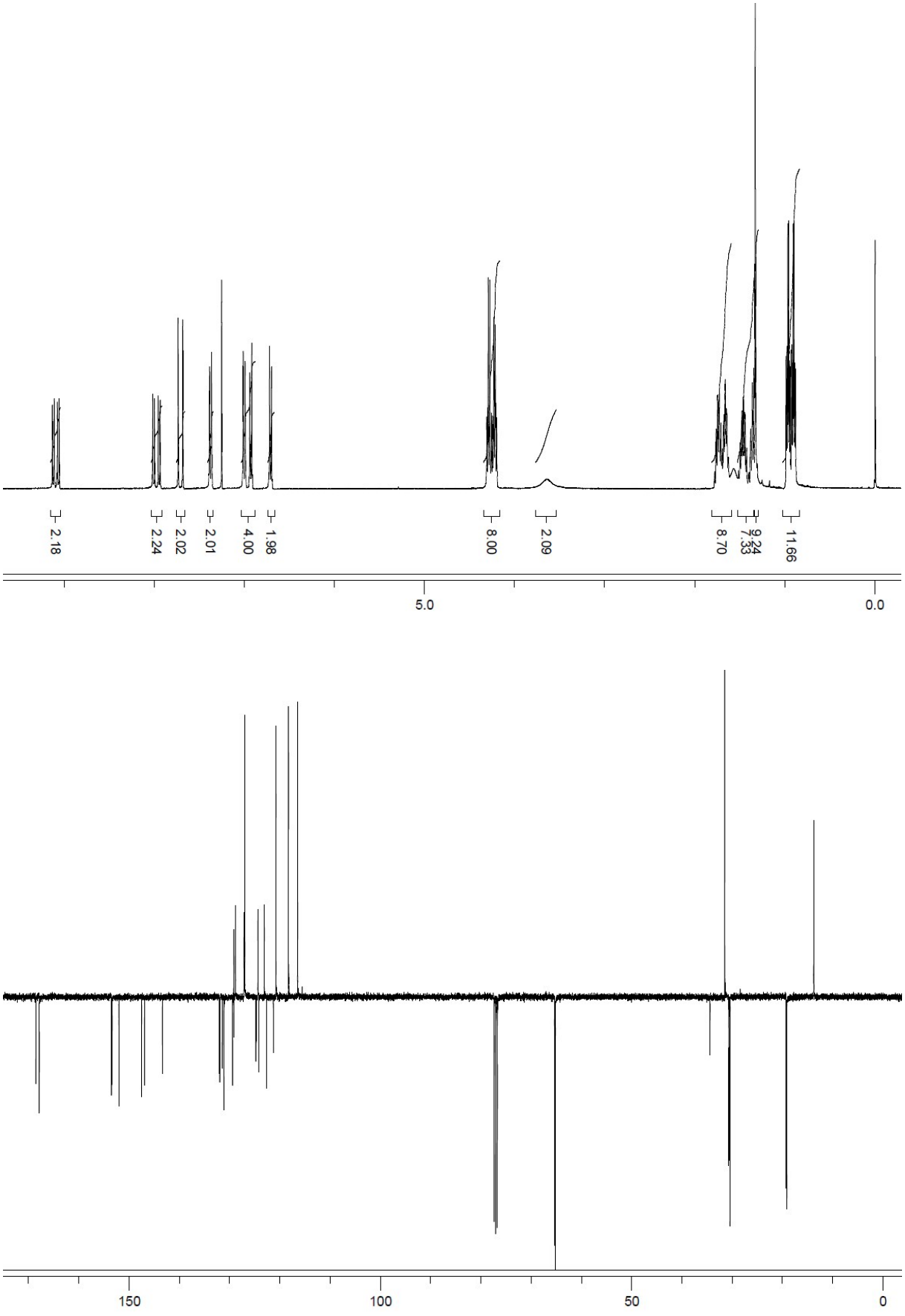


Figure S9. ^{1}H and ^{13}C NMR spectra of 1-(4-aminophenoxy)-7-(4-*tert*-butylphenoxy)perylene-3,4,9,10-tetracarboxy tetrabutylester (2b) in $CDCl_3$.

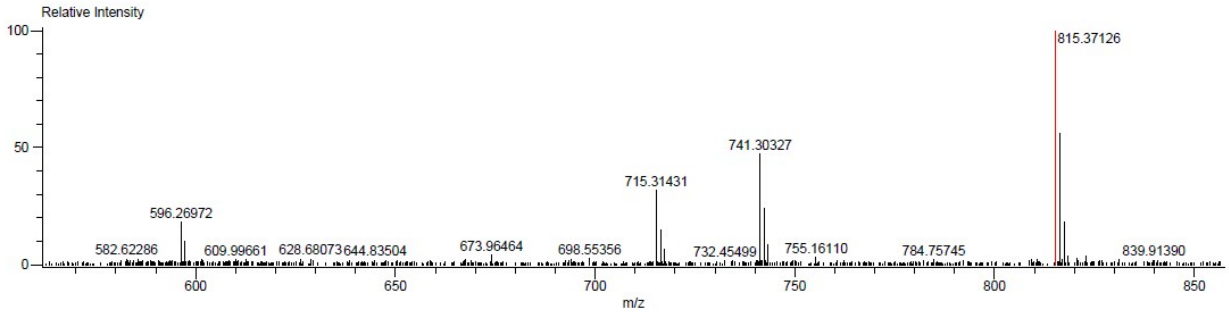
Data:W-J-3_10
Comment:
Description:
Ionization Mode:FD+(eiFi)
History:Centroid[Peak Detect[Centroid,30,Area]];Average(MS[1] 0.48..0.49)

Acquired:3/10/2015 11:14:32 AM
Operator:Accutof
m/z Calibration File:Calib_6okt2014_01
Created:3/10/2015 11:24:10 AM
Created by:Accutof

Charge number:1
Element:^{12}C:40 .. 60, ^{1}H:20 .. 100, ^{14}N:0 .. 4, ^{16}O:2 .. 14

Tolerance:6.00[ppm]

Unsaturation Number:-1.5 .. 60.0 (Fraction:Both)



Mass	Intensity	Calc. Mass	Mass Difference [ppm]	Possible Formula	^{12}C	^{1}H	^{14}N	^{16}O	Unsaturation Number
815.37126	39437.13	815.37148	-0.26	$^{12}C_{40}{}^{1}H_{55}{}^{14}N_{4}{}^{16}O_{14}$	40	55	4	14	15.5
		815.37550	-5.20	$^{12}C_{45}{}^{1}H_{55}{}^{14}N_{2}{}^{16}O_{12}$	45	55	2	12	19.5
		815.36695	5.29	$^{12}C_{49}{}^{1}H_{53}{}^{14}N_{1}{}^{16}O_{10}$	49	53	1	10	24.0
		815.36963	2.01	$^{12}C_{52}{}^{1}H_{51}{}^{14}N_{2}{}^{16}O_{7}$	52	51	2	7	28.5
		815.37231	-1.28	$^{12}C_{55}{}^{1}H_{49}{}^{14}N_{3}{}^{16}O_{4}$	55	49	3	4	33.0
		815.37365	-2.93	$^{12}C_{57}{}^{1}H_{51}{}^{16}O_{5}$	57	51		5	32.5

Figure S10. High resolution mass spectrum of compound 1a.

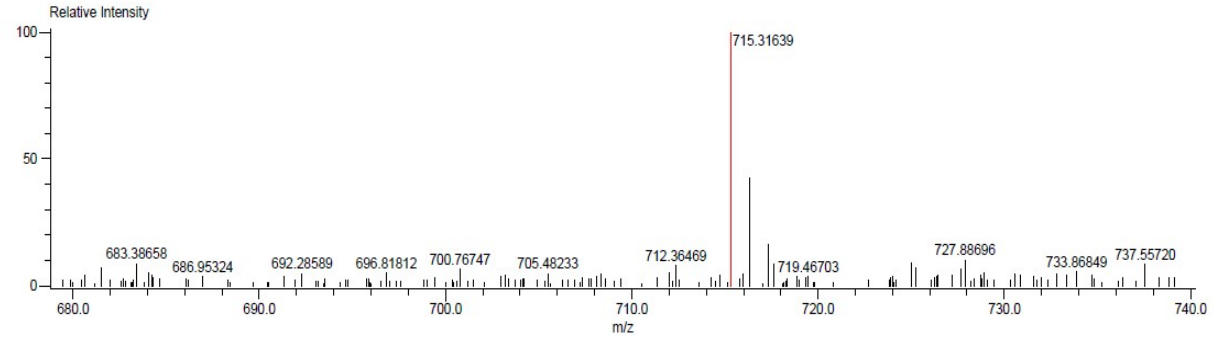
Data:W-J-2_10
Comment:
Description:
Ionization Mode:FD+(eiFi)
History:Centroid[Peak Detect[Centroid,30,Area]];Average(MS[1] 0.41..0.43)

Acquired:3/10/2015 11:02:17 AM
Operator:Accutof
m/z Calibration File:Calib_6okt2014_01
Created:3/10/2015 11:07:35 AM
Created by:Accutof

Charge number:1
Element:^{12}C:40 .. 60, ^{1}H:20 .. 100, ^{14}N:0 .. 4, ^{16}O:2 .. 14

Tolerance:5.00[ppm]

Unsaturation Number:-1.5 .. 60.0 (Fraction:Both)



Mass	Intensity	Calc. Mass	Mass Difference [ppm]	Possible Formula	^{12}C	^{1}H	^{14}N	^{16}O	Unsaturation Number
715.31639	10913.82	715.31317	4.50	$^{12}C_{42}{}^{1}H_{43}{}^{14}N_{4}{}^{16}O_{7}$	42	43	4	7	23.5
		715.31452	2.62	$^{12}C_{44}{}^{1}H_{45}{}^{14}N_{1}{}^{16}O_{8}$	44	45	1	8	23.0
		715.31720	-1.13	$^{12}C_{47}{}^{1}H_{43}{}^{14}N_{2}{}^{16}O_{5}$	47	43	2	5	27.5
		715.31988	-4.87	$^{12}C_{50}{}^{1}H_{41}{}^{14}N_{3}{}^{16}O_{2}$	50	41	3	2	32.0

Figure S11. High resolution mass spectrum of compound 1b.

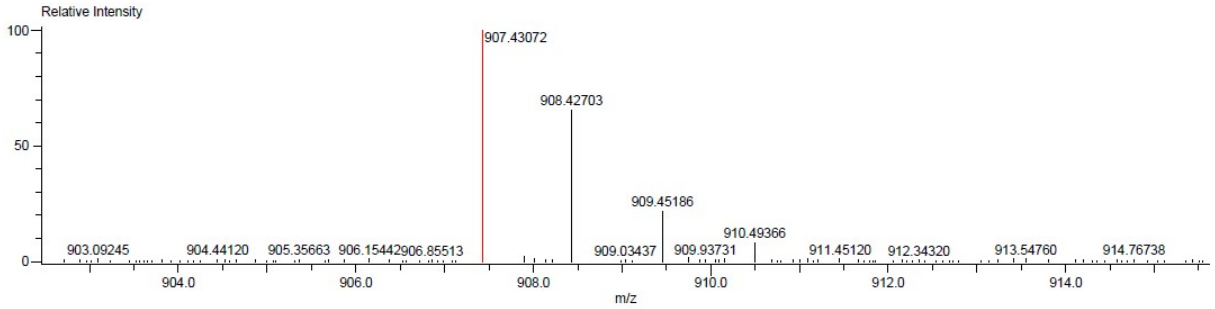
Data:RD-546-PTBE-NH2_03
Comment:
Description:
Ionization Mode:FD+(eiFi)
History:Centroid[Peak Detect[Centroid,30,Area]];Average(MS[1] 0.74..0.74)

Acquired:9/1/2015 1:43:11 PM
Operator:Accutof
m/z Calibration File:Calib_10aug15
Created:9/1/2015 1:49:05 PM
Created by:Accutof

Charge number:1
Element:^{12}C:25 .. 100, ^{1}H:10 .. 100, ^{14}N:0 .. 4, ^{16}O:0 .. 20

Tolerance:5.00[ppm]

Unsaturation Number:-1.5 .. 80.0 (Fraction:Both)



Mass	Intensity	Calc. Mass	Mass Difference [ppm]	Possible Formula	^{12}C	^{1}H	^{14}N	^{16}O	Unsaturation Number
907.43072	51639.75	907.42872	2.21	$^{12}C_{41}{}^{1}H_{67}{}^{14}N_{2}{}^{16}O_{20}$	41	67	2	20	9.5
		907.43140	-0.74	$^{12}C_{44}{}^{1}H_{65}{}^{14}N_{3}{}^{16}O_{17}$	44	65	3	17	14.0
		907.43274	-2.22	$^{12}C_{46}{}^{1}H_{67}{}^{16}O_{18}$	46	67		18	13.5
		907.43408	-3.69	$^{12}C_{47}{}^{1}H_{63}{}^{14}N_{4}{}^{16}O_{14}$	47	63	4	14	18.5
		907.42686	4.25	$^{12}C_{53}{}^{1}H_{63}{}^{16}O_{13}$	53	63		13	22.5
		907.42820	2.78	$^{12}C_{54}{}^{1}H_{59}{}^{14}N_{4}{}^{16}O_{9}$	54	59	4	9	27.5
		907.42955	1.30	$^{12}C_{56}{}^{1}H_{61}{}^{14}N_{1}{}^{16}O_{10}$	56	61	1	10	27.0
		907.43223	-1.66	$^{12}C_{59}{}^{1}H_{59}{}^{14}N_{2}{}^{16}O_{7}$	59	59	2	7	31.5
		907.43491	-4.61	$^{12}C_{62}{}^{1}H_{57}{}^{14}N_{3}{}^{16}O_{4}$	62	57	3	4	36.0
		907.42635	4.82	$^{12}C_{66}{}^{1}H_{55}{}^{14}N_{2}{}^{16}O_{2}$	66	55	2	2	40.5
		907.43038	0.38	$^{12}C_{71}{}^{1}H_{55}$	71	55			44.5

Figure S12. High resolution mass spectrum of compound 2b.

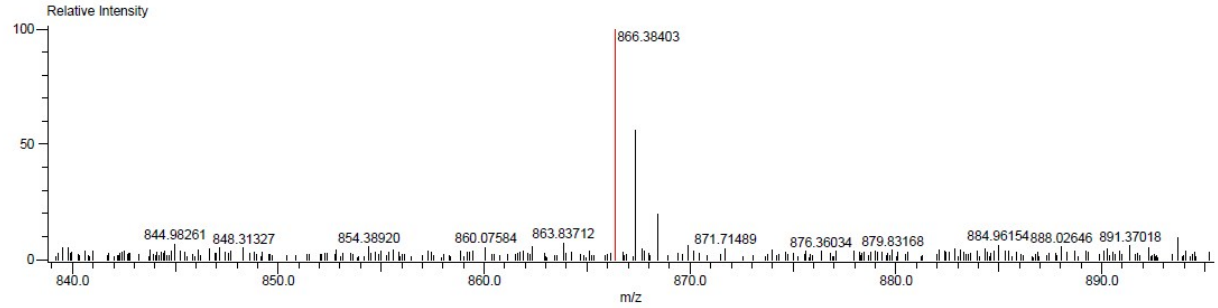
Data:W-J-4_10
Comment:
Description:
Ionization Mode:FD+(eiFi)
History:Centroid[Peak Detect[Centroid,30,Area]];Average(MS[1] 0.53..0.53)

Acquired:3/10/2015 11:30:40 AM
Operator:Accutof
m/z Calibration File:Calib_6okt2014_01
Created:3/10/2015 11:34:05 AM
Created by:Accutof

Charge number:1
Element:^{12}C:40 .. 60, ^{1}H:20 .. 100, ^{14}N:0 .. 4, ^{16}O:2 .. 14

Tolerance:10.00[ppm]

Unsaturation Number:-1.5 .. 60.0 (Fraction:Both)



Mass	Intensity	Calc. Mass	Mass Difference [ppm]	Possible Formula	^{12}C	^{1}H	^{14}N	^{16}O	Unsaturation Number
866.38403	16971.00	866.38640	-2.73	$^{12}C_{48}{}^{1}H_{56}{}^{14}N_{3}{}^{16}O_{12}$	48	56	3	12	22.5
		866.38774	-4.28	$^{12}C_{50}{}^{1}H_{58}{}^{16}O_{13}$	50	58		13	22.0
		866.38908	-5.83	$^{12}C_{51}{}^{1}H_{54}{}^{14}N_{4}{}^{16}O_{9}$	51	54	4	9	27.0
		866.37784	7.14	$^{12}C_{52}{}^{1}H_{54}{}^{14}N_{2}{}^{16}O_{10}$	52	54	2	10	27.0
		866.39042	-7.38	$^{12}C_{53}{}^{1}H_{56}{}^{14}N_{1}{}^{16}O_{10}$	53	56	1	10	26.5
		866.38052	4.05	$^{12}C_{55}{}^{1}H_{52}{}^{14}N_{3}{}^{16}O_{7}$	55	52	3	7	31.5
		866.38187	2.50	$^{12}C_{57}{}^{1}H_{54}{}^{16}O_{8}$	57	54		8	31.0
		866.38320	0.95	$^{12}C_{58}{}^{1}H_{50}{}^{14}N_{4}{}^{16}O_{4}$	58	50	4	4	36.0
		866.38455	-0.60	$^{12}C_{60}{}^{1}H_{52}{}^{14}N_{1}{}^{16}O_{5}$	60	52	1	5	35.5

Figure S13. High resolution mass spectrum of compound 3.

References:

[1] S. Sengupta, R. K. Dubey, R. W. M. Hoek, S. P. P. van Eeden, D. D. Gunbaş, F. C. Grozema, E. J. R. Sudhölter, W. F. Jager. *J. Org. Chem.* 2014, **79**, 6655–6662.

[2] H. Choi, M. Song, Y. Sim, H. Bae, J. Kim, L. Park. *Mol. Cryst. Liq. Cryst.* 2010, **531**, 47–54.

[3] Quantum yield determination were performed using perylene-3,4,9,10-tetracarboxylic acid tetrapotassium salt as a reference, see: H. Langhals, J. Karolin, L. B-Å. Johansson. *J. Chem. Soc., Faraday Trans*., 1998, **94**, 2919.

[4] J. R. Lakowicz, Principles of Fluorescence Spectroscopy; Kluwer Academic and Plenum Publishers: New York, 1999.

[5] R. H. Mach, S. Vangveravong, Y. Huang, B. Yang, J. B. Blair, L. Wu, *Med. Chem. Res*. 2993, 11, 380-398.

[6] The reaction was first carried out with unprotected 4-aminophenol, which produced ~50% of **3** and significant amounts of de-bromination compounds.

[7] F. Jahani, M. Tajbakhsh, H. Golchoubian, S. Khaksar. *Tetrahedron Lett*, 2011, **52**, 1260-1264.