Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Electronic Supporting Information

For

Synthesis and Photophysical Properties of Pyrene-Based Green Fluorescent Dyes: Butterfly-Shaped Architectures

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General Methods:

^{1}H NMR spectra were recorded on Bruker ACF300 (300 MHz) spectrometer. The chemical shifts were reported in ppm and referenced to the residual solvent peak. s = singlet, d = doublet, t = triplet, m = multiplet, b = broad. FAB-mass spectra were obtained on a Finnigan MAT95XL-T, MALDI-TOF on Bruker Autoflex III and Micromass VG7035 mass spectrometer. The UV-Vis and emission spectra were measured on a UV-1601PC Shimadzu spectrophotometer and RF-5301PC Shimadzu spectrofluorophotometer. Bruker ALPHA FT-IR Spectrophotometer was used for the Fourier transform infrared (FT-IR) spectroscopy analysis. Good quality crystal was obtained from a two-phase solvent system where the compound first was dissolved in a $CHCl_3$ and transferred in NMR tube. Next, hexane in which compound is not soluble, was poured slowly in such way that it form two solvent layers and it was kept for few days without disturbing until the crystal was obtained. The structure of the compound was determined by X-ray crystal diffraction. Geometry optimizations were performed in Gaussian 09 at the density functional theory (DFT) level with the B3LYP functional and a 6-31G(d) basis set. The HOMO and LUMO surfaces were generated from the optimized geometries using GaussView 5.

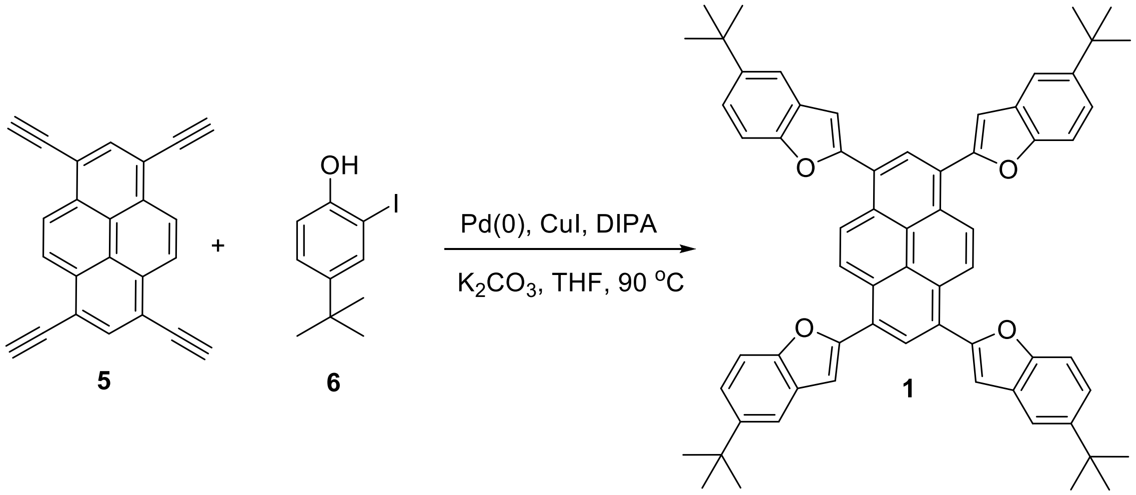
General Procedure for palladium catalyzed cross-coupling reaction

A 50 mL Schlenk flask equipped with a stir bar was charged with compound 1,3,6,8-tetraethynyl pyrene **5**[1] (1 eq.), Iodo aryl derivative (5.0 eq.) and copper(I)iodide (0.4 eq.). The flask was placed under argon, and tetrakis(triphenylphosphine)palladium(0) (0.4 eq.) and K_2CO_3 (5 eq.) were added under a nitrogen atmosphere. Tetrahydrofuran and diisopropylamine in 1: 3 ratio were added by syringe, the mixture was degassed for 20 min, and heated at 90°C for 12 hours. The reaction mixture was cooled, diluted with water, and extracted with EtOAc. The organic layer was washed with brine, dried over anhyd. Na_2SO_4, filtered, concentrated, and purified on a silica gel column to afford the target compound.

Synthetic Procedure:

1,3,6,8-tetrakis(5-tert-butylbenzofuran-2-yl)pyrene (1).

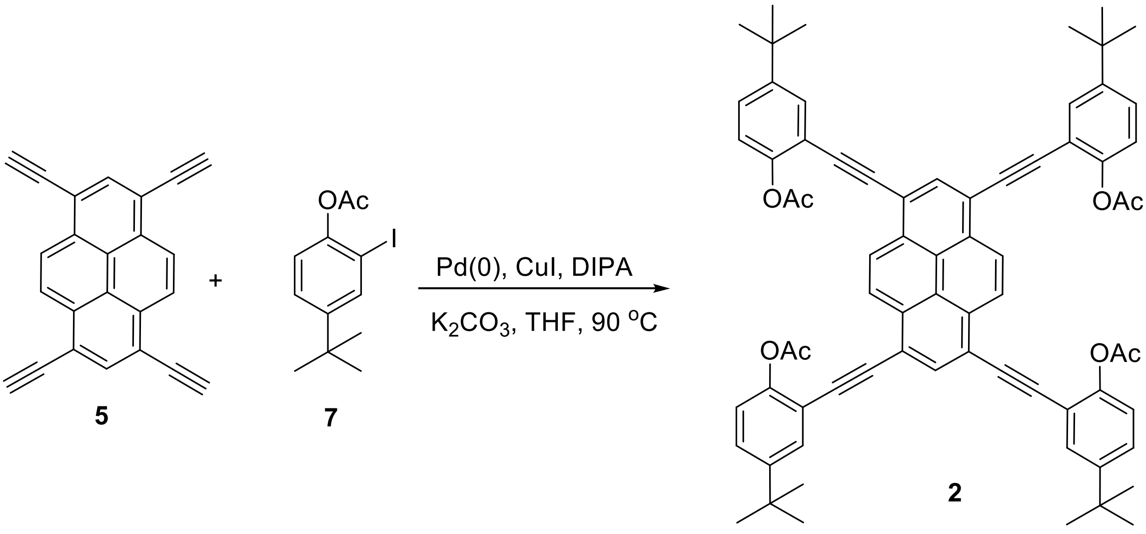
Compound **5**[1] and **6**[2] were synthesized according to the literature procedure.



Following the general procedure for palladium catalyzed cross-coupling reaction, starting from 1,3,6,8-tetraethynyl pyrene **5** (0.3 g, 1 mmol), 4-*tert*-butyl,2-Iodophenol **6** (1.38 g, 5 mmol) and copper(I)iodide (0.076 g, 0.4 mmol), tetrakis(triphenylphosphine)palladium(0) (0.46 g, 0.4 mmol) and K_2CO_3 (0.69 g, 5 mmol), the compound **1** (0.63 g, 71%) was afforded as a orange solid after silica gel flash column chromatography (5% ethylacetate in hexanes). R_f = 0.8 (1:9 ethyl acetate/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.80 (s, 3H, Ar), 8.75 (s, 2H, Ar), 7.76 (d, *J* = 1.8 Hz, 4H, Ar), 7.60 (d, *J* = 8.5 Hz, 4H, Ar), 7.50 (dd, *J* = 1.8, 8.5 Hz, 4H, Ar), 7.28 (s, 4H, Ar), 1.49 (s, 36H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.4, 153.5, 146.2, 128.8, 128.2, 127.6, 126.1, 125.8, 125.7, 122.6, 117.3, 110.7, 107.5, 34.8, 31.9; MALDI-TOF: ($C_{64}H_{58}O_4$) Calculated m/z = 890.43, Found m/z = 890.73; IR (KBr): ν = 2958, 2925, 1858, 1464, 1264, 1092, 1024, 805.

2,2',2'',2'''-(pyrene-1,3,6,8-tetrayltetrakis(ethyne-2,1-diyl))tetrakis(4-tert-butylbenzene-2,1-diyl) tetraacetate (2).

Compound **7**[2] was synthesized by following the literature procedure.

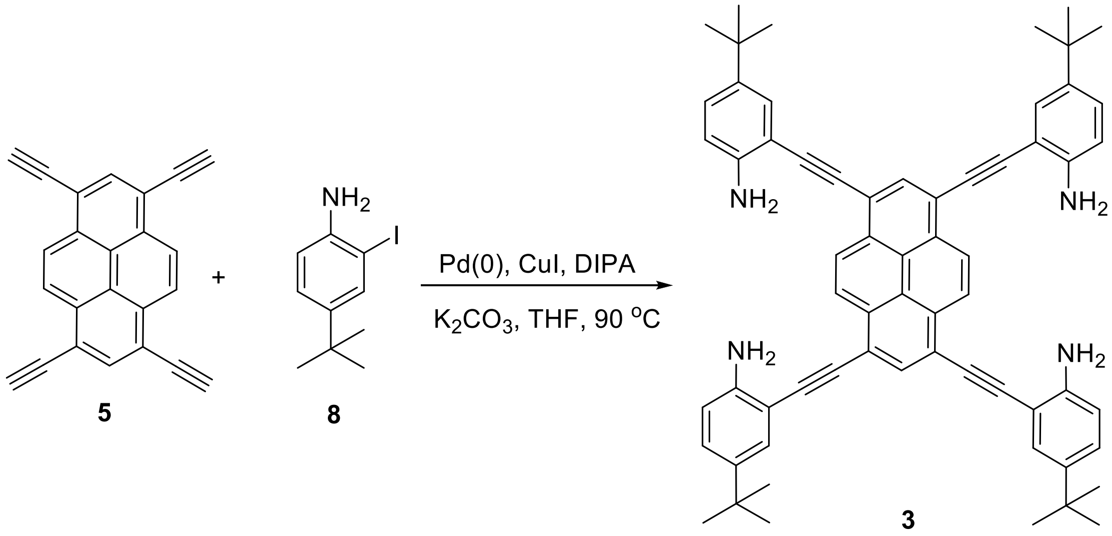


Following the general procedure for palladium catalyzed cross-coupling reaction, starting from 1,3,6,8-tetraethynyl pyrene **5** (0.3 g, 1 mmol), 4-*tert*-butyl-2-iodophenyl acetate **7**

(1.59 g, 5 mmol) and copper(I)iodide (0.076 g, 0.4 mmol), tetrakis(triphenylphosphine)palladium(0) (0.46 g, 0.4 mmol) and K_2CO_3 (0.69 g, 5 mmol), the compound **2** (0.83 g, 79%) was afforded as a orange-yellow solid after silica gel flash column chromatography (25% ethylacetate in hexanes). $R_f = 0.4$ (2:8 ethyl acetate/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.77 (s, 4H, Ar), 8.44 (s, 2H, Ar), 7.77 (d, *J* = 2.5 Hz, 4H, Ar), 7.48 (dd, *J* = 2.5, 8.5 Hz, 4H, Ar), 7.15 (d, *J* = 8.5 Hz, 4H, Ar), 2.46 (s, 12H), 1.40 (s, 36H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.2, 149.3, 149.1, 133.7, 131.8, 130.1, 127.3, 126.9, 121.8, 118.9, 116.3, 91.7, 91.4, 34.5, 31.3, 21.1.; MALDI-TOF: ($C_{72}H_{66}O_8$) Calculated m/z = 1058.47, Found m/z = 1058.78; IR (KBr): ν = 3054, 2959, 2925, 2865, 2205 ($-C\equiv C-$), 1766, 1603, 1498, 1366, 1185.

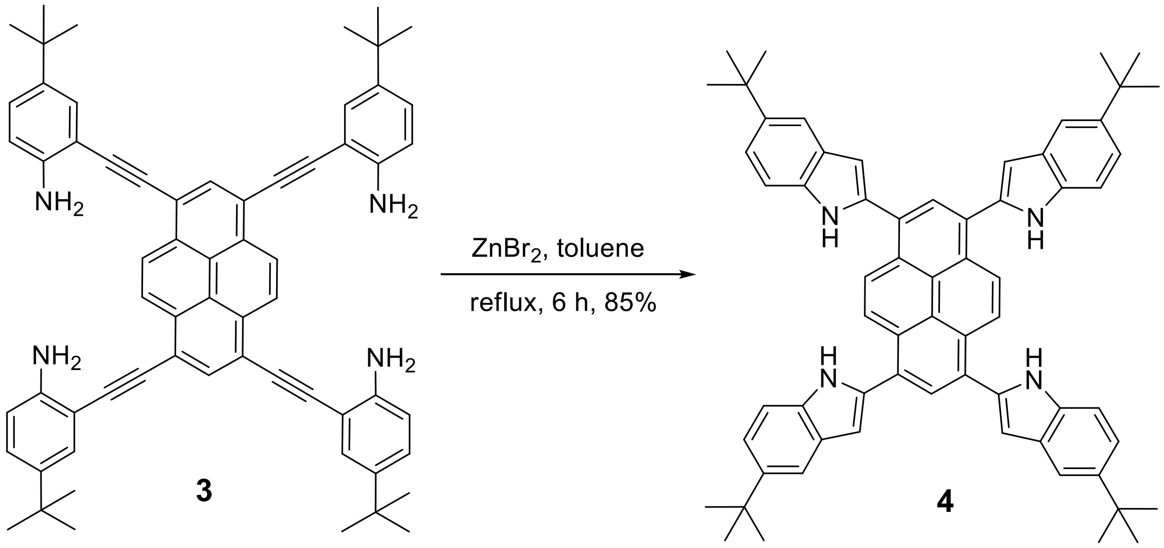
2,2',2'',2'''-(pyrene-1,3,6,8-tetrayltetrakis(ethyne-2,1-diyl))tetrakis(4-tert-butylaniline) (3).

Compound **8**[3] was synthesized according to the literature procedure.



Following the general procedure for palladium catalyzed cross-coupling reaction, starting from 1,3,6,8-tetraethynyl pyrene **5** (0.3 g, 1 mmol), 4-*tert*-butyl-2-iodoaniline **8** (1.37 g, 5 mmol) and copper(I)iodide (0.076 g, 0.4 mmol), tetrakis(triphenylphosphine)palladium(0) (0.46 g, 0.4 mmol) and K_2CO_3 (0.69 g, 5 mmol), the compound **2** (0.74 g, 83%) was afforded as a red solid after silica gel flash column chromatography (25% ethylacetate in hexanes). $R_f = 0.5$ (2:8 ethyl acetate/hexanes); ^{1}H NMR (300 MHz, acetone-d_6): δ 8.83 (s, 4H, Ar), 8.60 (s, 2H, Ar), 7.59 (d, J = 2.3 Hz, 4H, Ar), 7.29 (dd, J = 2.3, 8.5 Hz, 4H, Ar), 6.85 (d, J = 8.5 Hz, 4H, Ar), 5.24 (s, 6H, NH_2), 1.34 (s, 36H); ^{13}C NMR (75 MHz, acetone-d_6): δ 149.1, 140.9, 135.1, 132.4, 130.1, 129.3, 128.3, 125.6, 121.1, 115.9, 107.6, 96.1, 93.2, 35.1, 32.5; MALDI-TOF: ($C_{64}H_{62}N_4$) Calculated m/z = 886.50, Found m/z = 886.74; IR (KBr): ν = 3609, 3471, 3382 (NH_2), 2955, 2862, 2363, 2186 ($-C\equiv C-$), 1616, 1498, 1258, 822.

1,3,6,8-tetrakis(5-tert-butyl-1H-indol-2-yl)pyrene (4):



To a solution of chromophore **3** (0.1 g, 0.112 mmol) dissolved in dry toluene (10 mL) was added anh.$ZnBr_2$ (0.2 g, 0.90 mmol) at RT under nitrogen atmosphere. The reaction mixture was refluxed for 6 h, cooled to RT, the solvent was removed under *vacuo* and the crude was subjected to silicagel column chromatography to give oragne-brown solid compound **4** (0.085 g, 85%). R_f = 0.5 (1:3 ethyl acetate/hexanes); ^{1}H NMR (300 MHz, acetone-d_6): δ 10.71 (s, 4H, NH), 8.83 (s, 4H), 8.54 (s, 2H), 7.74 (s, 4H), 7.48 (d, *J* = 8.5 Hz, 4H), 7.36 (d, *J* = 8.5 Hz, 4H), 7.01 (s, 4H), 1.44 (s, 36H); ^{13}C NMR (75 MHz, acetone-d_6): δ 142.3, 136.6, 129.0, 128.7, 128.0, 125.7, 120.3, 116.1, 110.7, 104.5, 34.2, 31.3; MALDI-TOF: ($C_{64}H_{62}N_4$) Calculated m/z = 886.50, Found m/z = 886.46; IR (KBr): ν = 3394, 3055, 2956, 2865, 1609, 1468, 1403, 1311, 1142, 802 cm^{-1}.

References

1. *(a)* S. Bernhardt, M. Kastler, V. Enkelmann, M. Baumgarten and K. Müllen, *Chem. Eur. J.* 2006, ***12***, 6117–6128; *(b)* H. Lu, Q. Wang, Z. Li, G. Lai, J. Jiang, and Z. Shen, *Org. Biomol. Chem.*, 2011, ***9***, 4558–4562.
2. T. Wang, Z.Y. Li, A. L. Xie, X. J. Yao, X. P. Cao and D. Kuck, *J. Org. Chem.* 2011, ***76***, 3231–3238.
3. *(a)* W.-W. Sy, *Synth. Commun*. 1992, ***22***, 3215–3219; *(b)* J. Iskra, S. Starber and M. Zupam, *Synthesis*, 2004, 1869–1879.

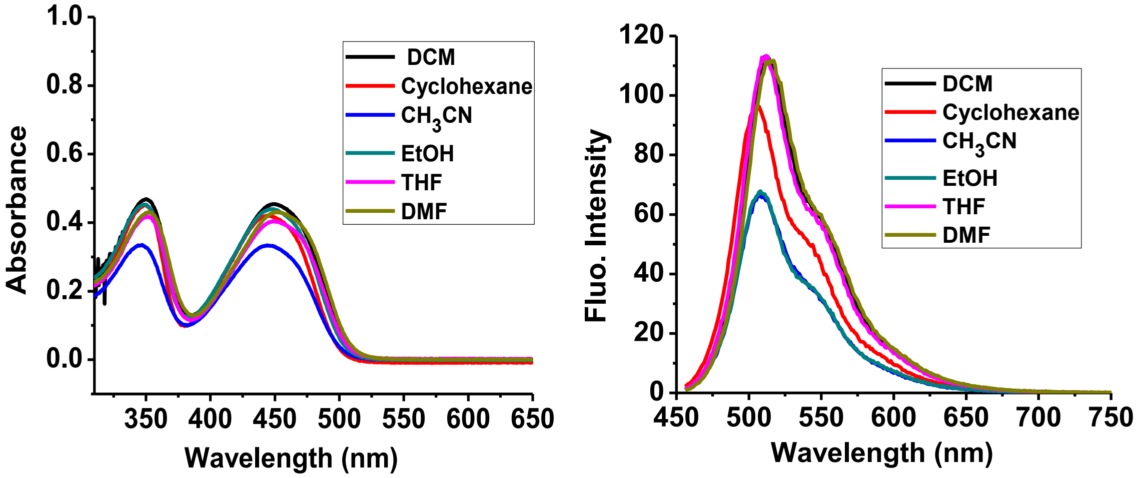


Figure S1. Absorbance in 10μM (left) and normalized fluorescence (right) in 1μM of compound **1**, recorded in different organic solvent.

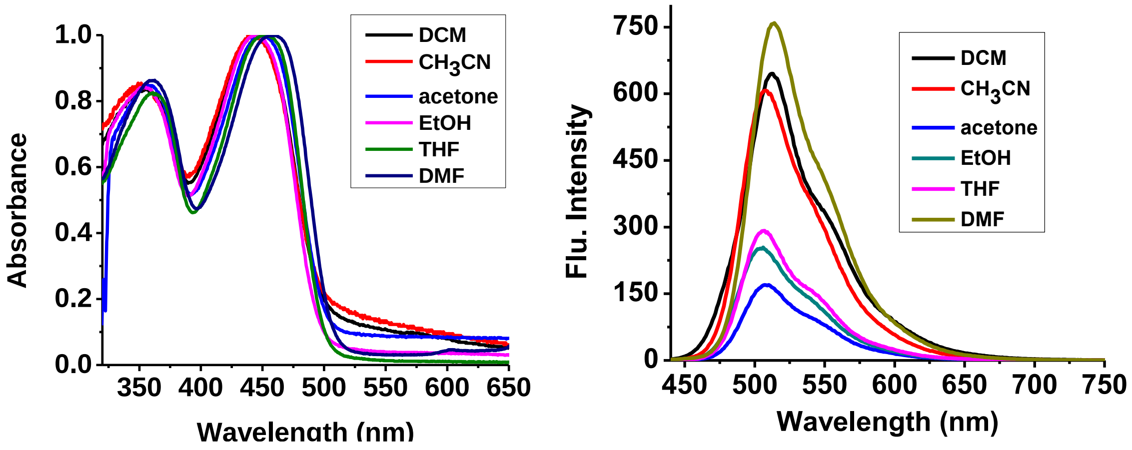


Figure S2. Absorbance in 10μM (left) and normalized fluorescence (right) in 1μM of compound **4**, recorded in different organic solvent.

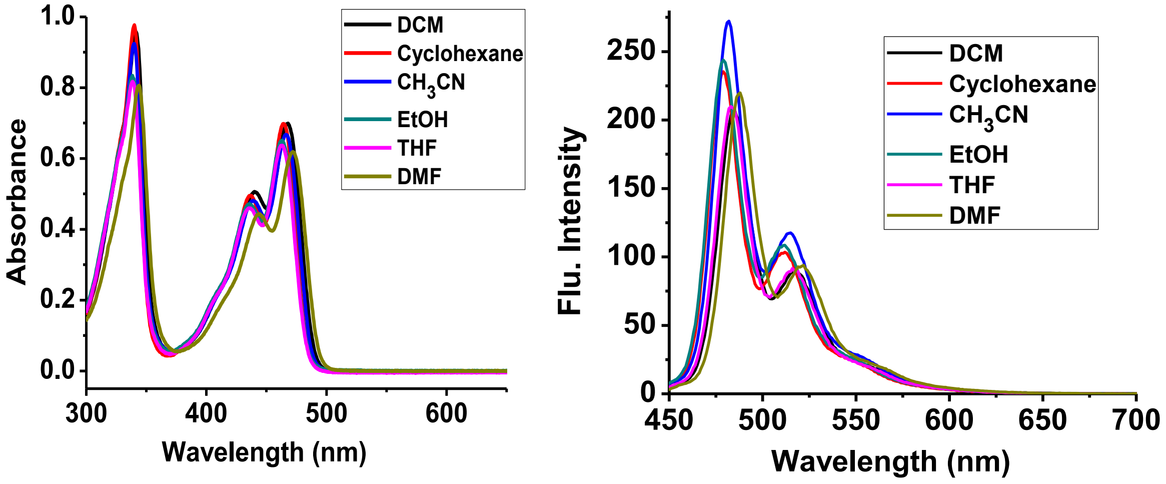


Figure S3. Absorbance spectra (left) and normalized fluorescence emission spectra (right) in different solvent system for compound **2** recorded at 25 ºC.

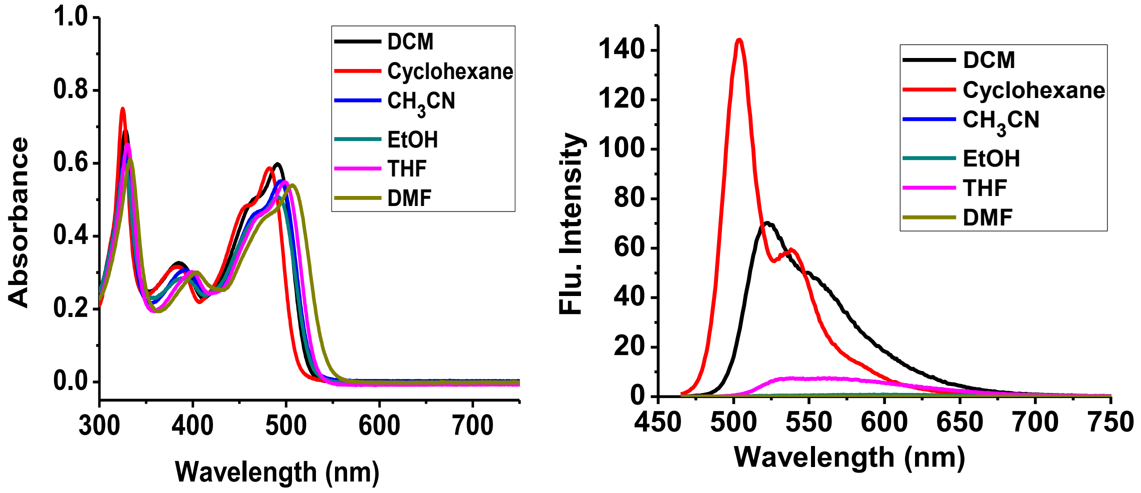


Figure S4. Absorbance spectra (left) and normalized fluorescence emission spectra (right) in different solvent system for compound **3** recorded at 25 ºC.

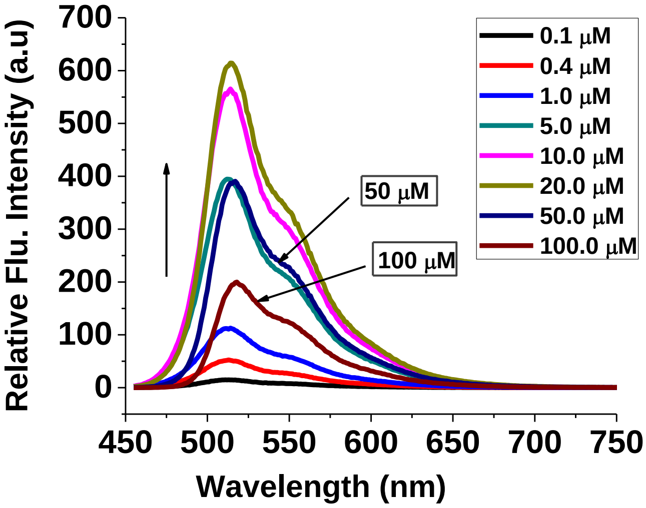


Figure S5. Effect of concentration on the fluorescence spectra for compound **1**, recorded in CH_2Cl_2 at 25 ºC upon increasing the concentration from 0.1μM to 100 μM.

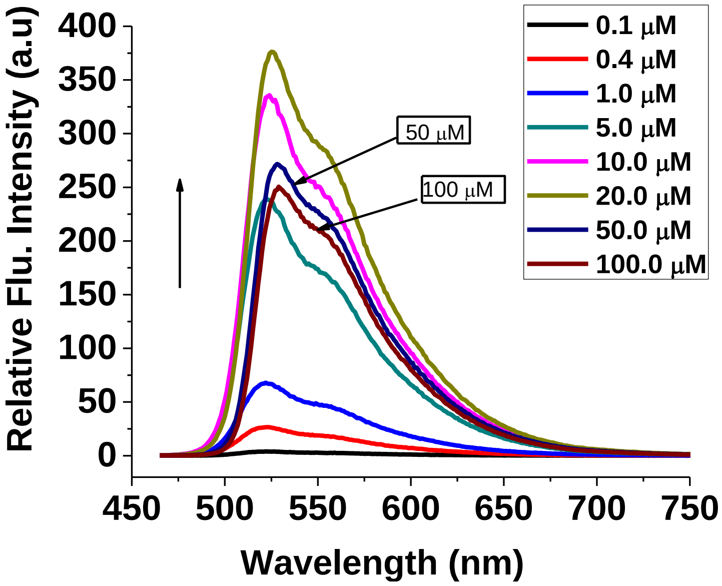


Figure S6. Effect of concentration on the fluorescence spectra for compound **3**, recorded in CH_2Cl_2 at 25 ºC upon increasing the concentration from 0.1μM to 100 μM.

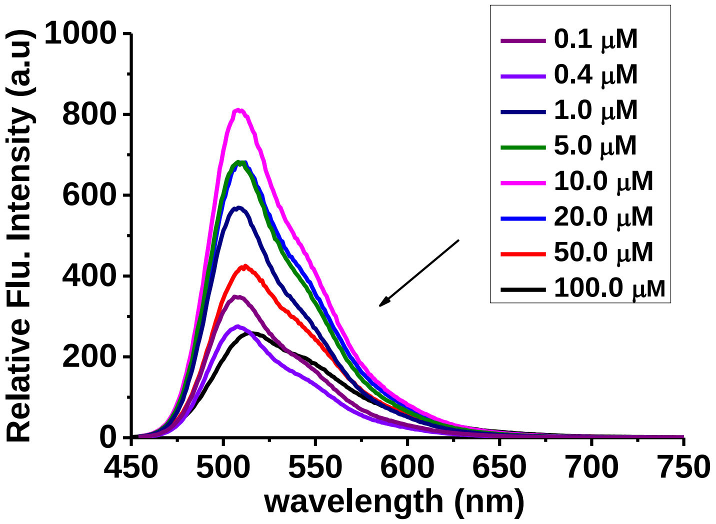


Figure S7. Effect of concentration on the fluorescence spectra for compound **4**, recorded in CH_2Cl_2 at 25 °C upon increasing the concentration from 0.1µM to 100 µM.

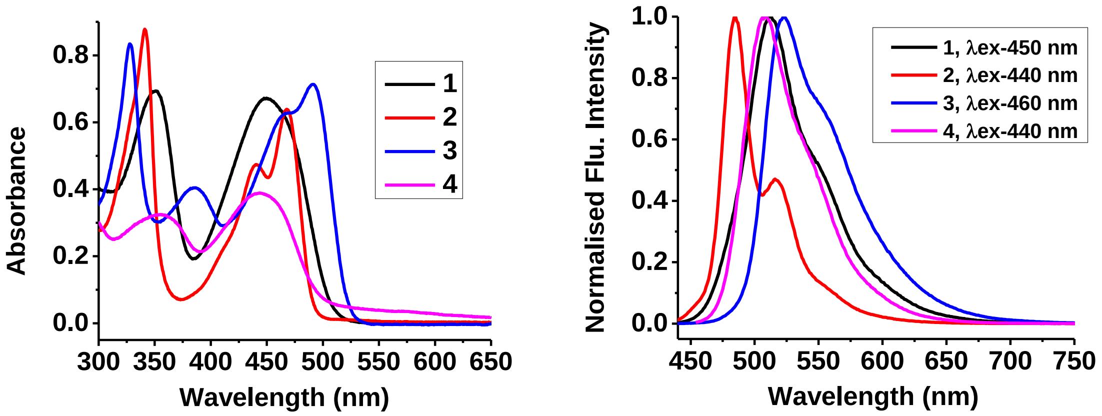
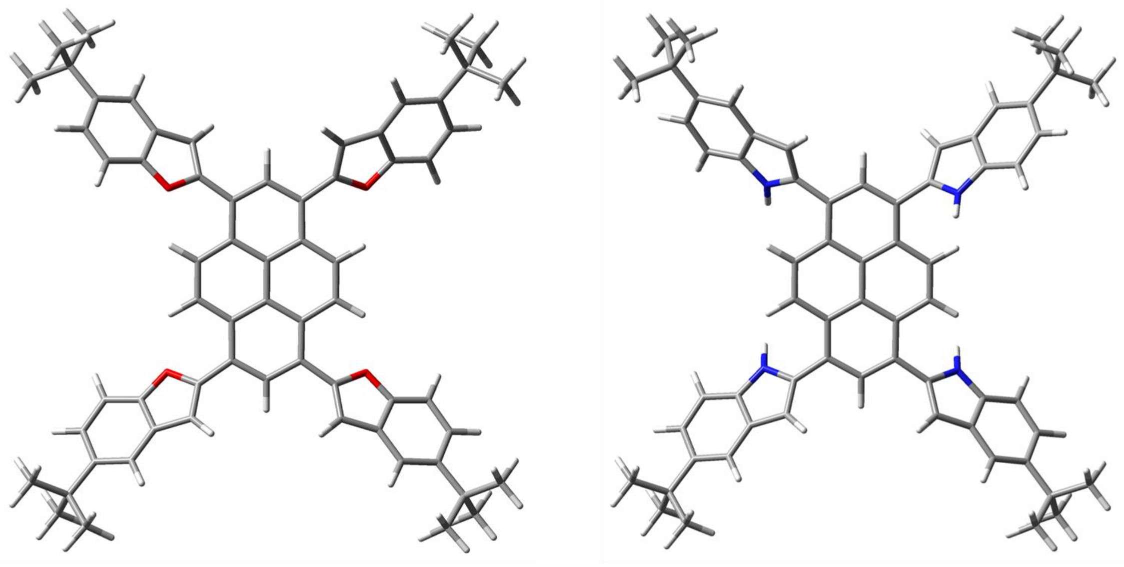


Figure S8. Absorbance in 10 µM (left) and normalized fluorescence in 1 µM of 1, 2, 3 and 4 recorded in CH_2Cl_2 solvent.



1

4

Figure S9. The energy optimized structure of **1** and **4** molecules calculated by density functional theory at the B3LYP/6-31G(d) level.

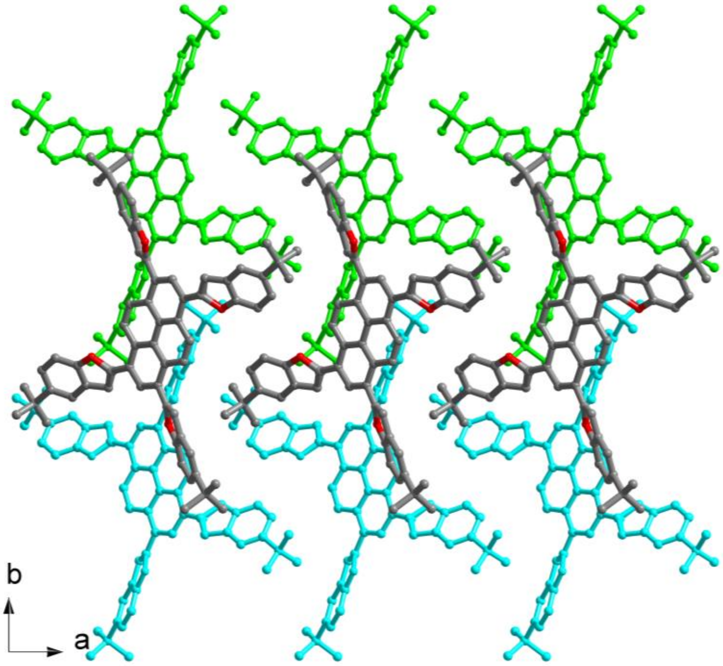


Figure S10. ORTEP representation of molecular packing viewed down the c axis of compound **1**

Table 1. Crystal data and structure refinement for D368N (**1**).

Identification code	d368n	
Empirical formula	C64 H58 O4	
Formula weight	891.10	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 12.291(2) Å	α= 90°.
	b = 17.310(3) Å	β= 95.536(5)°.
	c = 11.563(2) Å	γ = 90°.
Volume	2448.7(8) Å^3	
Z	2	
Density (calculated)	1.209 Mg/m^3	
Absorption coefficient	0.074 mm^{-1}	
F(000)	948	
Crystal size	0.46 x 0.26 x 0.10 mm^3	
Theta range for data collection	1.66 to 25.00°.	
Index ranges	-13<=h<=14, -18<=k<=20, -13<=l<=10	
Reflections collected	14069	
Independent reflections	4314 [R(int) = 0.0543]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6393	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4314 / 127 / 351	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0775, wR2 = 0.1815	
R indices (all data)	R1 = 0.1044, wR2 = 0.1964	
Largest diff. peak and hole	0.583 and -0.458 e.Å^{-3}	

compd	$CHCl_3$	EtOH	THF	DMSO
1	0.80	0.78	0.81	0.74
2	0.89	0.61	0.84	0.69
3	0.64	0.20	0.40	0.04
4	0.74	0.59	0.73	0.66

Table 2: Quantum yields of compounds **1**, **2**, **3**, and **4** measured in $CHCl_3$, EtOH, THF, and DMSO solvents

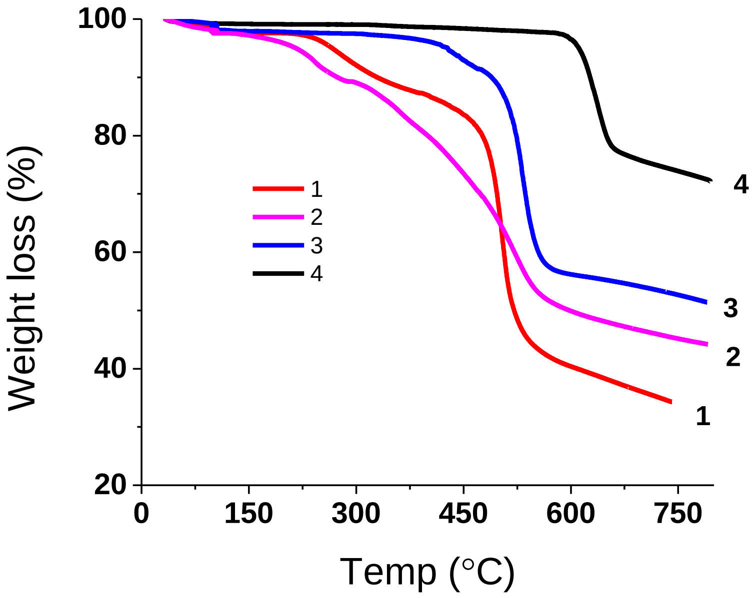


Figure S11. Thermogravimetry analysis for compound **1**, **2**, **3** and **4**

Fluorophores	**Decomposition temperature[a] °C**
1	**320**
2	**264**
3	**480**
4	**625**

[a] Decomposition temperature was measured at 10% weight loss of fluorophore

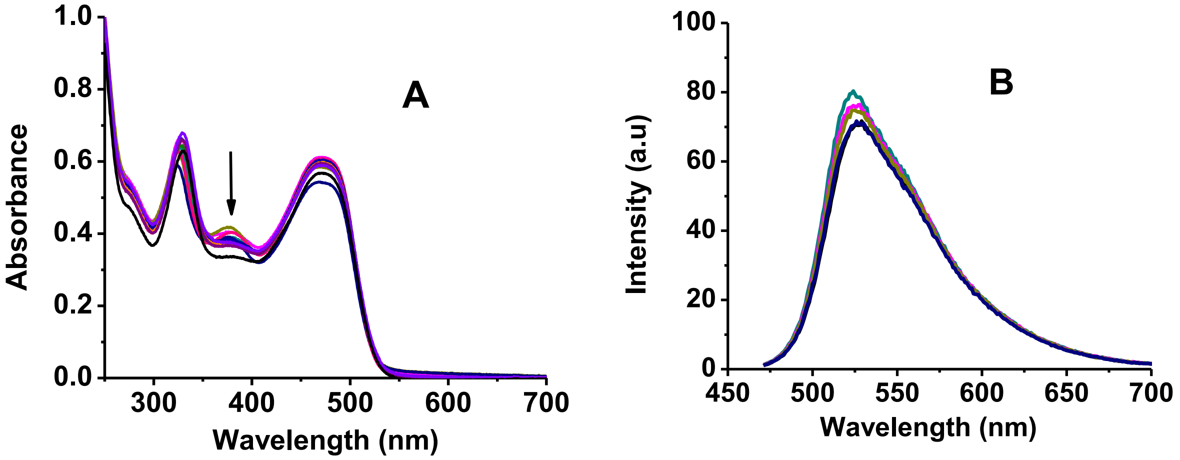


Fig.12. The absorption (A) and emission spectra (B) of compound **3** (10 μM) in the presence of H^+ ions in EtOH. Compound **3** was titrated with acid from pH 6, 5, 4, 3, and 2 (No changes were observed)

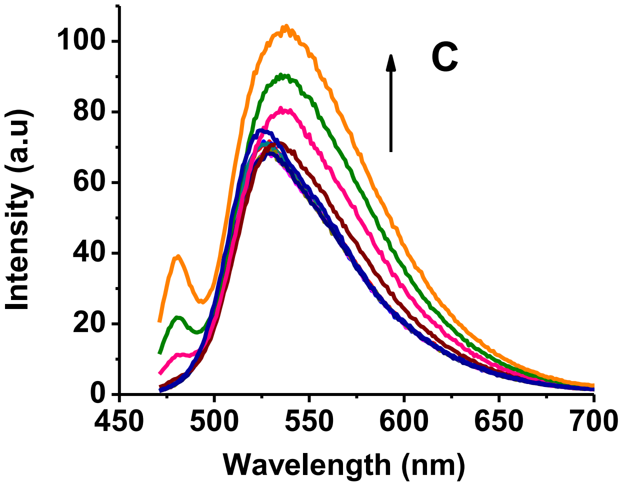
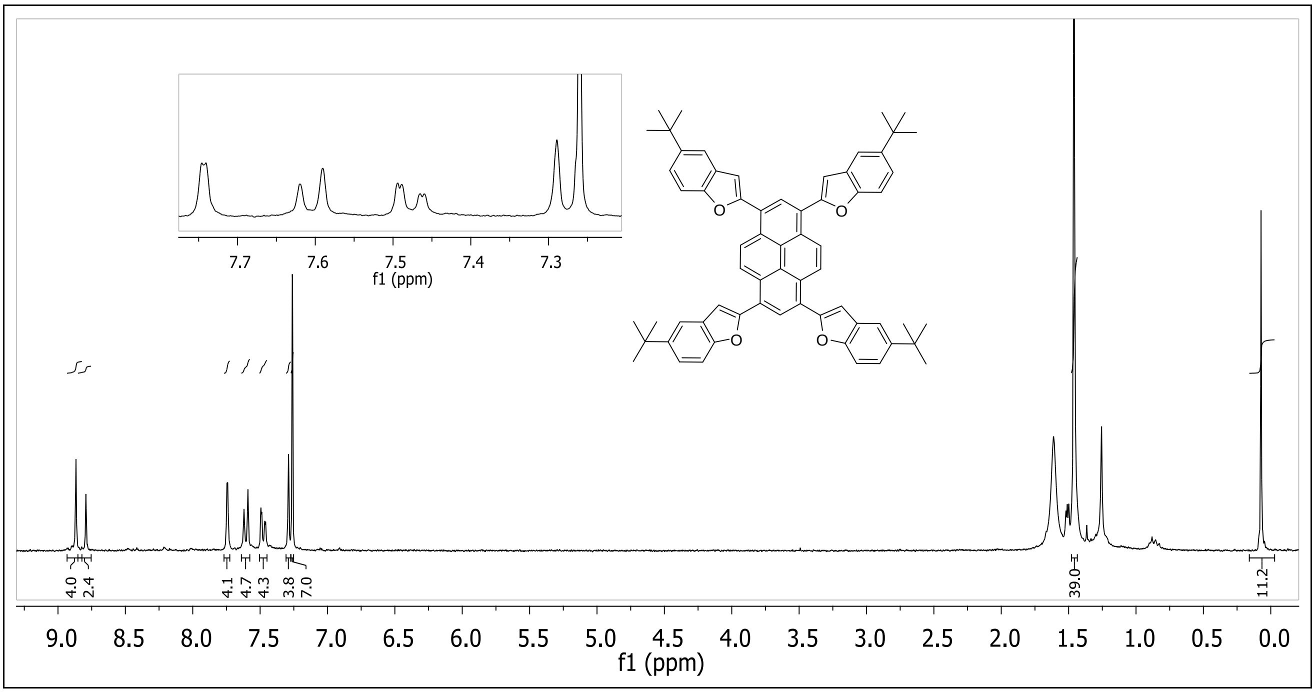


Fig.13. The emission spectra (C) of compound **3** (10 μM) in the presence of H^+ ions in EtOH. Compound **3** was titrated with acid from pH 2, 1.8, 1.6, 1.4, 1.2, 1, 0.8, 0.6, and 0.2 respectively. (Changes were observed)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8.5
8.0
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7.0
6.5
6.0
5.5
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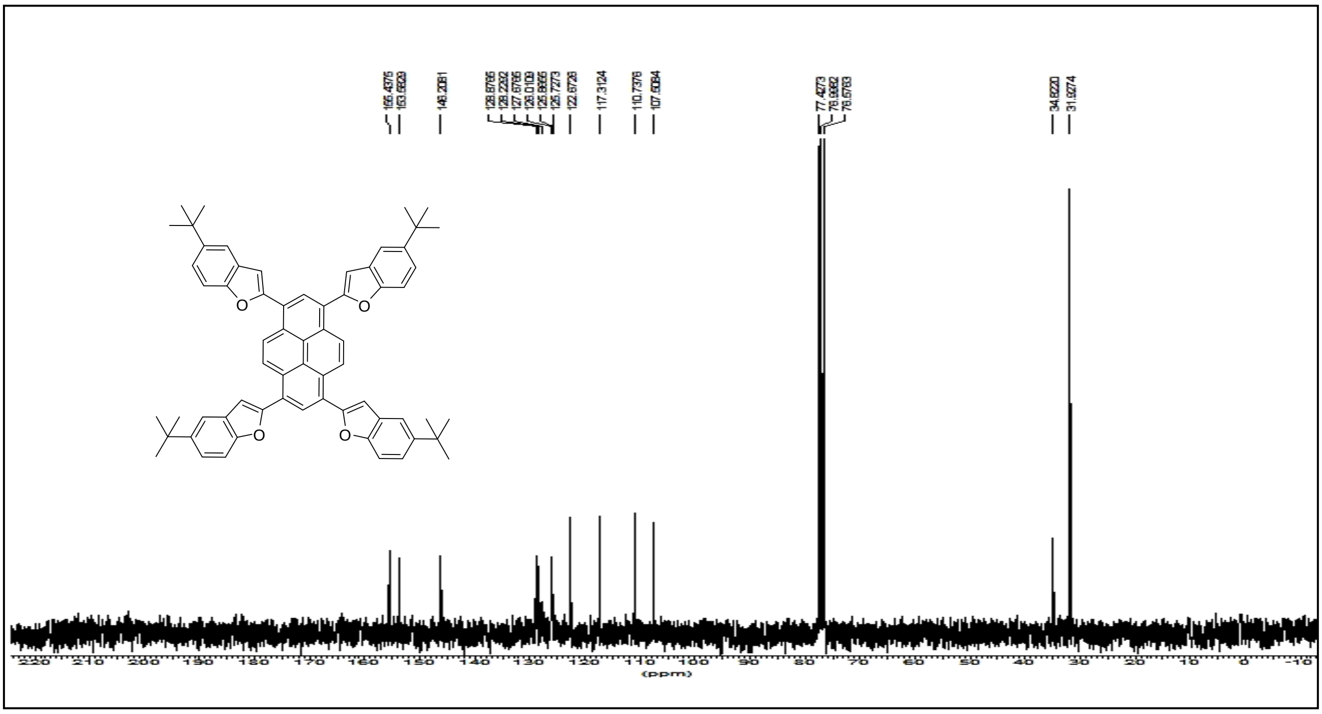
0.0
f1 (ppm)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77.4273
76.9992
76.5763
34.8220
31.9274
O
O
O
O
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210
200
190
180
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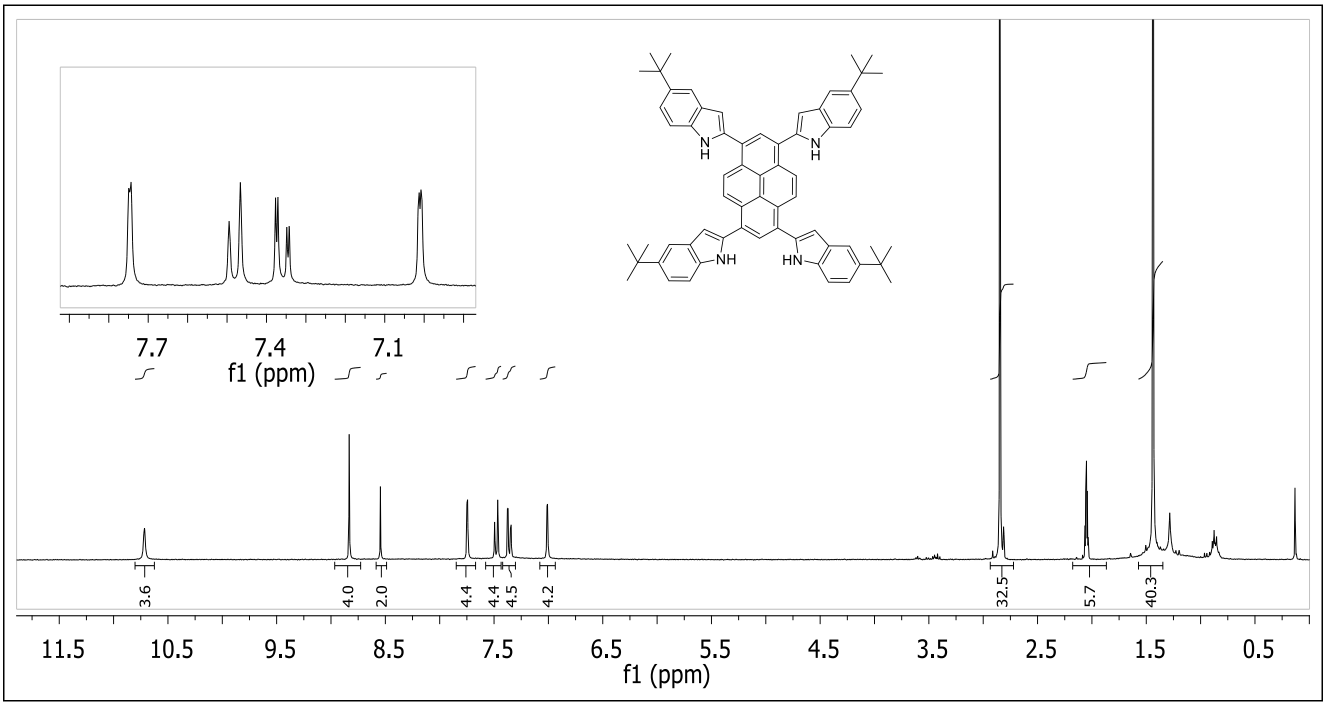
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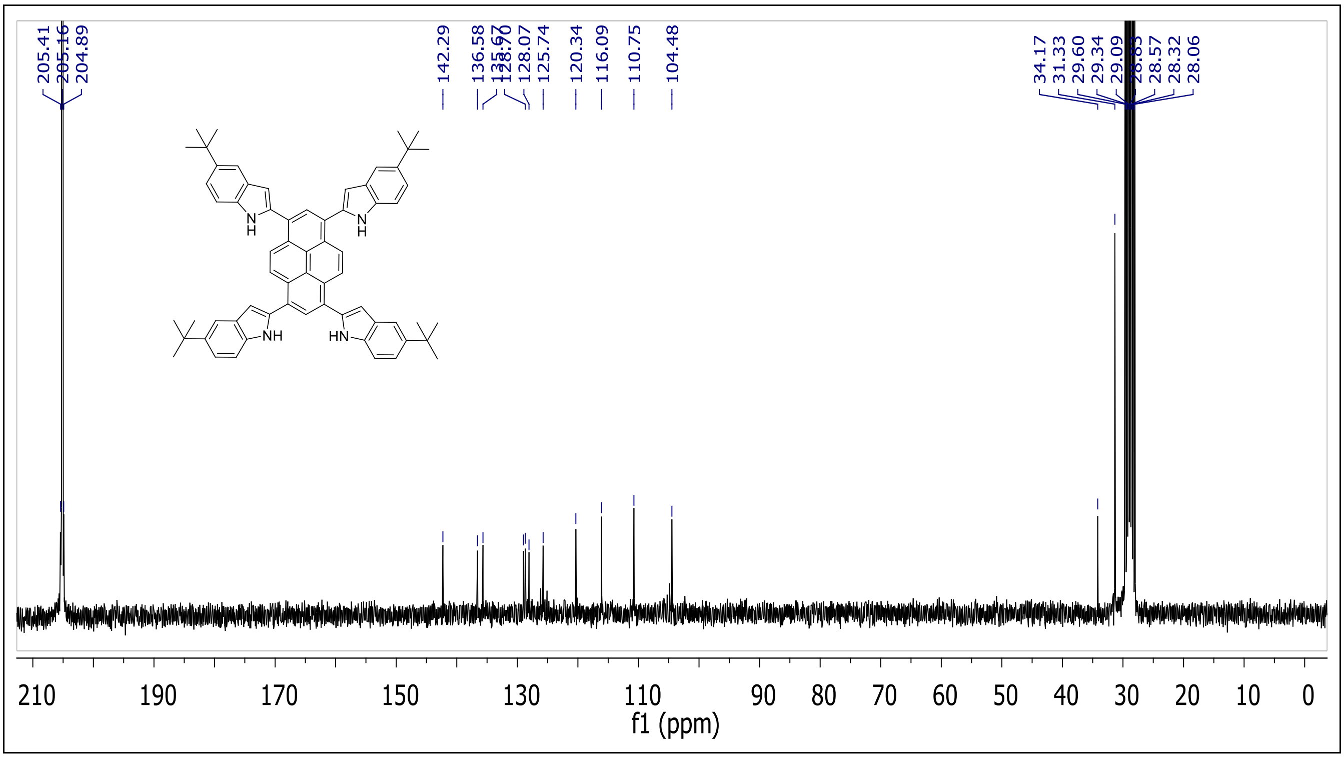
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31.33
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28.57
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H
H
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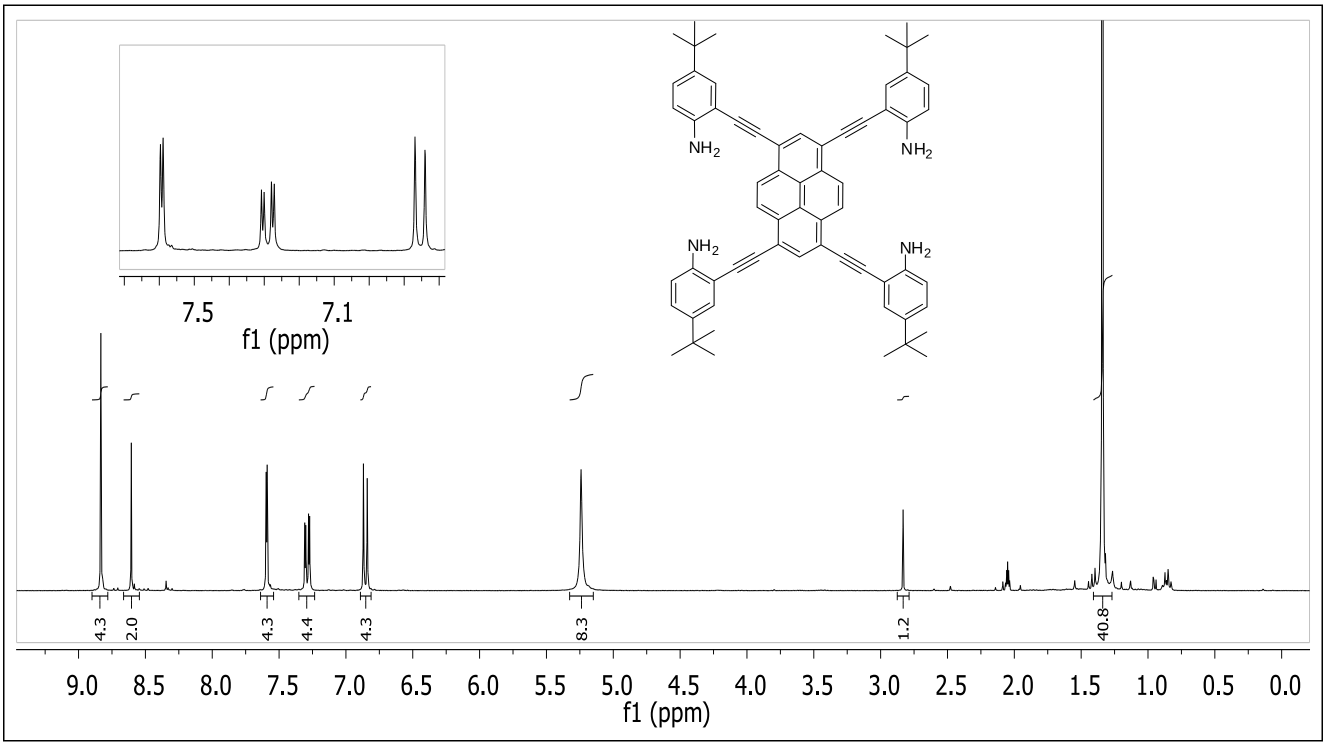
50
40
30
20
10
0
f1 (ppm)



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NH2
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f1 (ppm)
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1.2
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8.0
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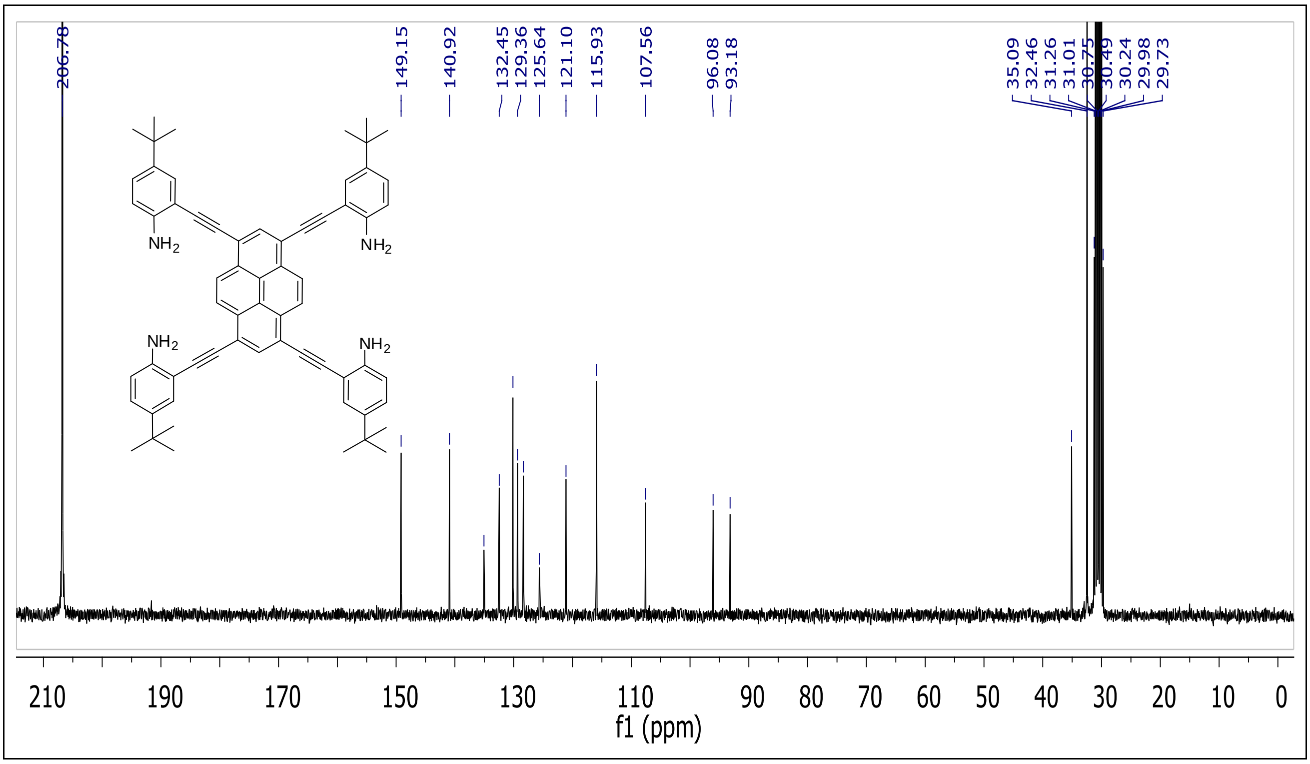
f1 (ppm)



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NH2
NH2
NH2
NH2
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150
130
110
90
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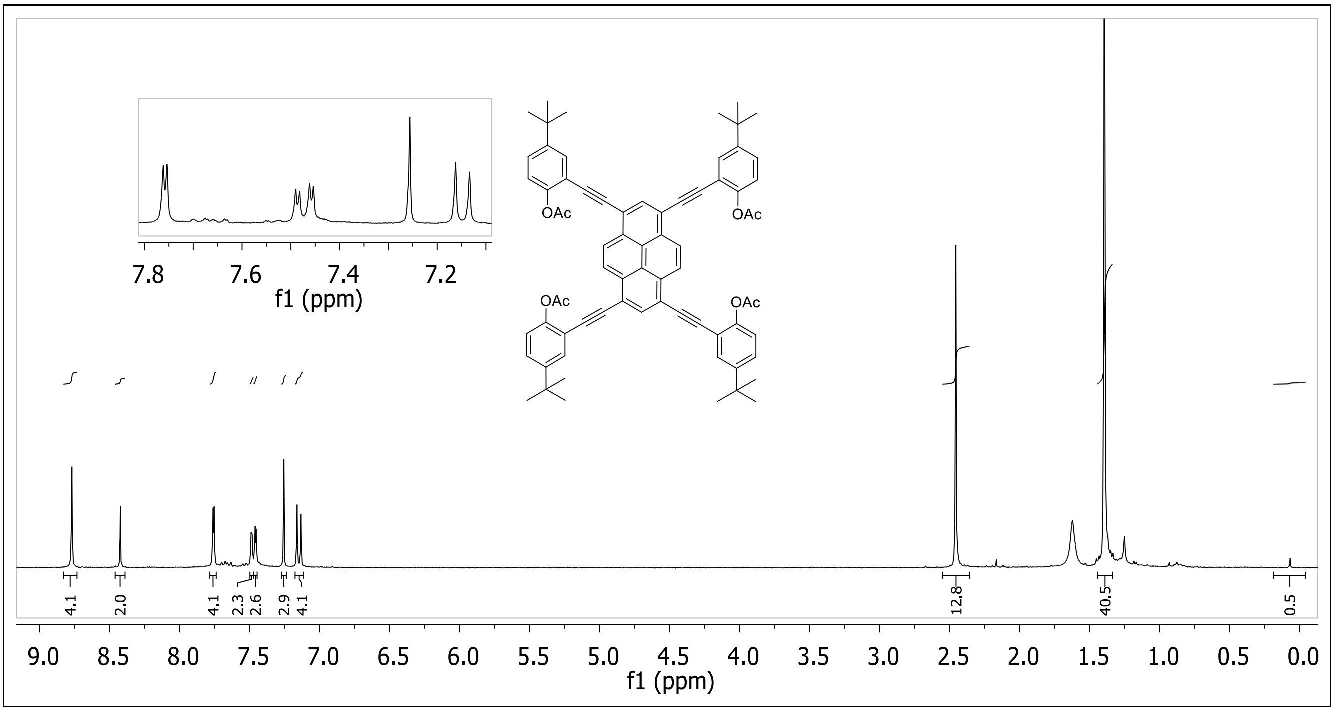
50
40
30
20
10
0
f1 (ppm)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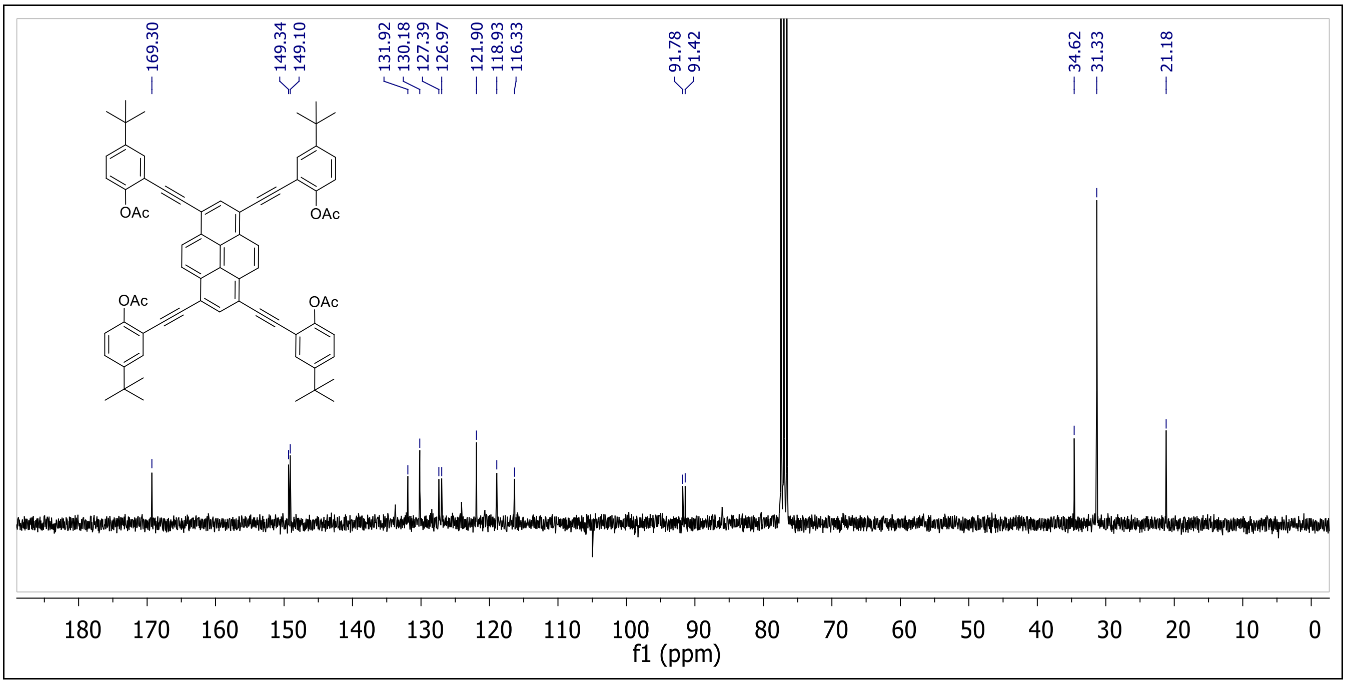
0.0
f1 (ppm)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OAc
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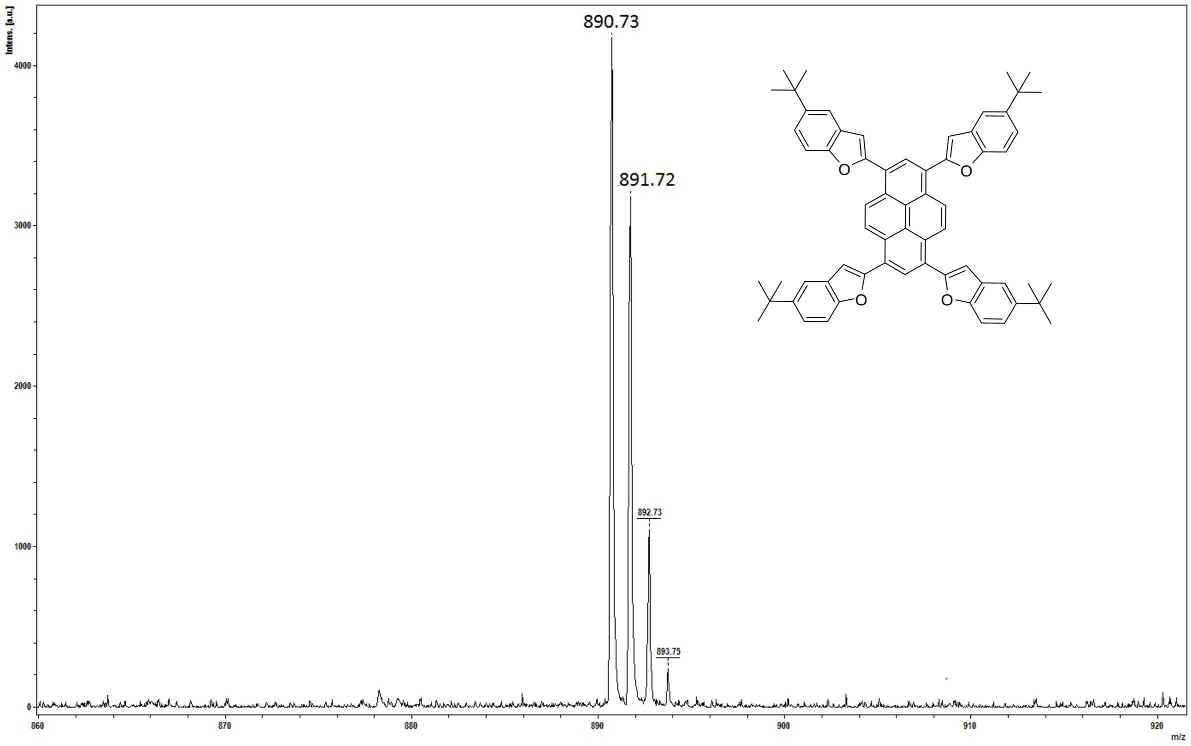
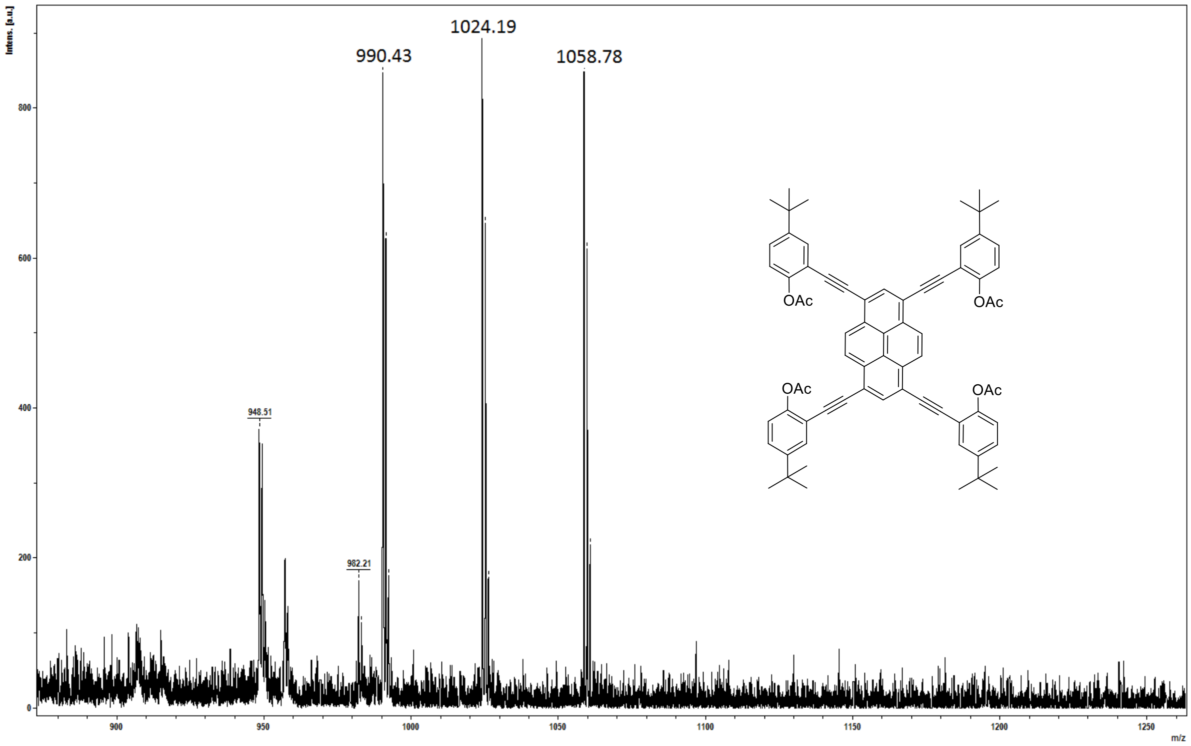
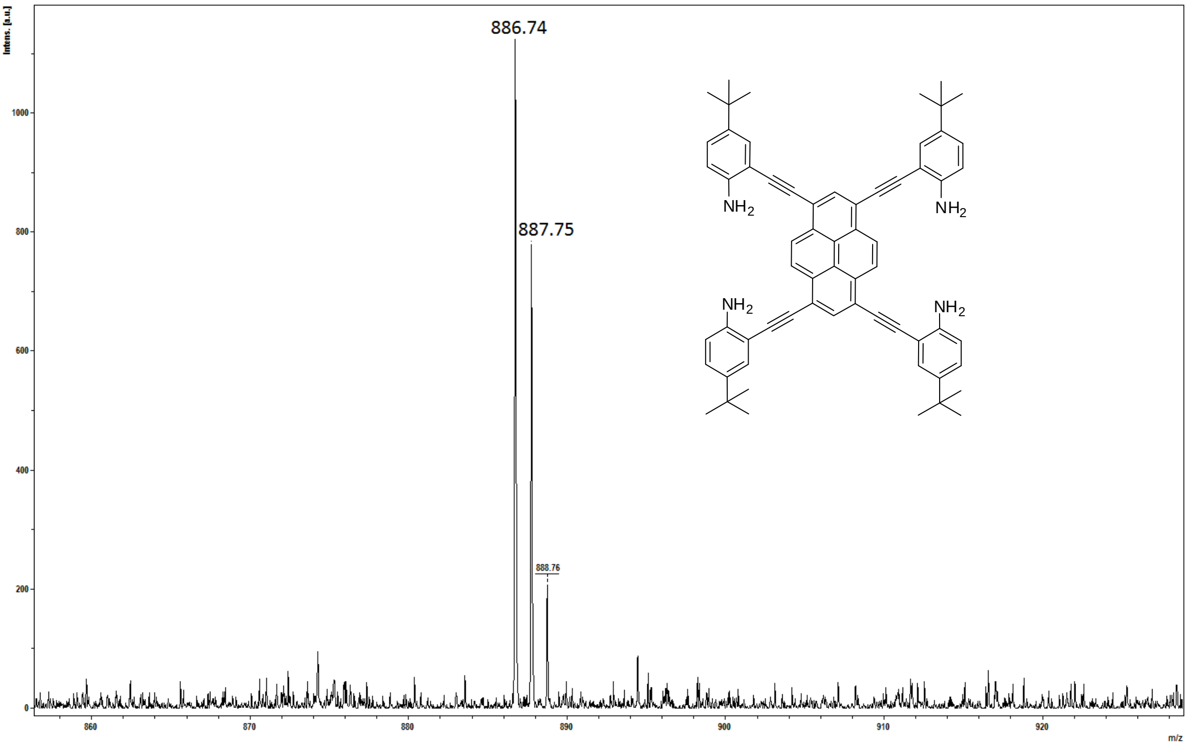
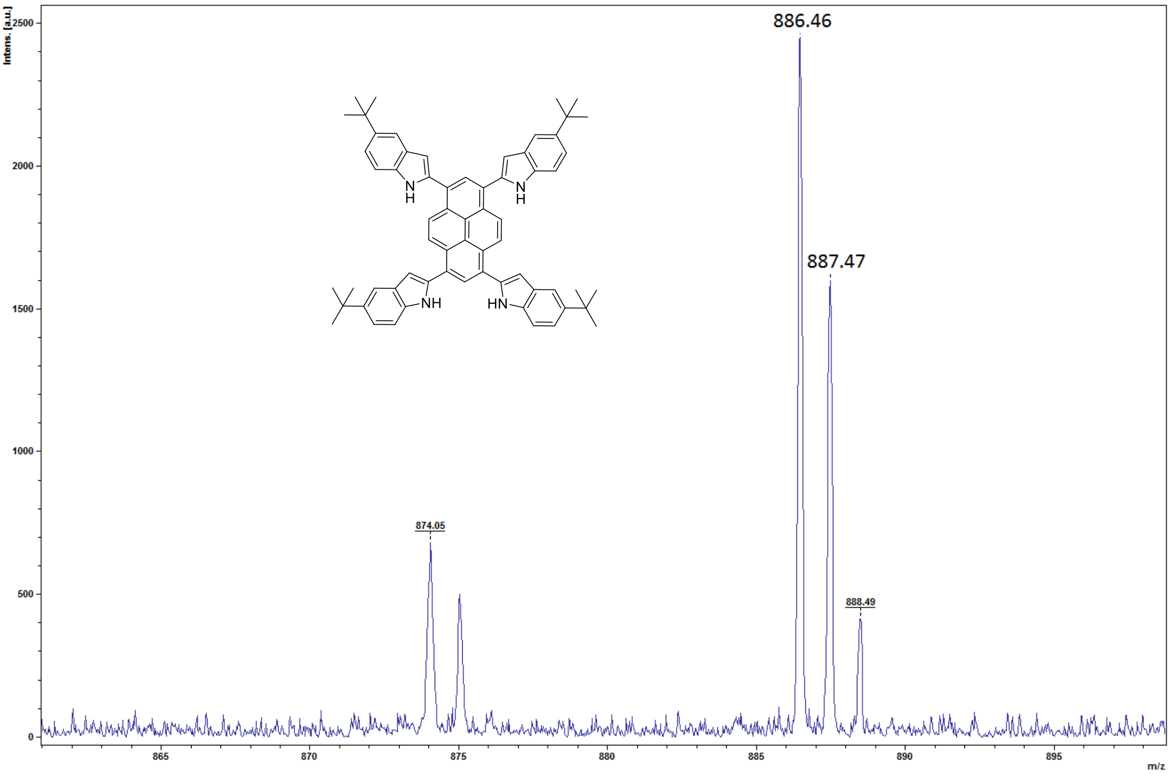
40
30
20
10
0
f1 (ppm)


Intens. [a.u.]
4000
3000
2000
1000
0
890.73
891.72
892.73
893.75
O
O
O
O
860
870
880
890
900
910
920
m/z


Intens. [a.u.]
800
600
400
200
0
1024.19
990.43
1058.78
948.51
982.21
OAc
OAc
OAc
OAc
900
950
1000
1050
1100
1150
1200
1250
m/z


Intens. [a.u.]
886.74
887.75
888.76
NH$_2$
NH$_2$
NH$_2$
NH$_2$
0
200
400
600
800
1000
860
870
880
890
900
910
920
m/z


Intens. [a.u.]
886.46
887.47
874.05
888.49
N H
N H
NH
HN
0
500
1000
1500
2000
2500
865
870
875
880
885
890
895
m/z