Electronic Supplementary Material (ESI) for ChemComm.

Layered assembly of cationic and anionic supramolecular polymers

Jovana Jevric, Simon M. Langenegger and Robert Häner

Content

1 Abbreviations

AFM	Atomic force microscope
APTES	(3-Aminopropyl)triethoxysilane
CEP-Cl	2-Cyanoethyl N,N-diisopropylchlorophosphoramidite
DCE	1,2-Dichloroethane
DCM	Dichloromethane
DIPEA	N,N-Diisopropylethylamine
DLS	Dynamic light scattering
Et_3N	Triethylamine
EtOAc	Ethyl acetate
MeOH	Methanol
RT	Room temperature
TEM	Transmission electron microscope
THF	Tetrahydrofuran
TLC	Thin-layer chromatography

2 General methods

All chemicals and solvents were purchased from commercial suppliers and used without further purification. 3,6-Dibromophenanthrene (**2**) was prepared according to literature.[1]

All NMR spectra were measured on a Bruker Avance III HD (300 MHz) spectrometer. Mass spectra were obtained on a Thermo Fisher LTQ Orbitrap XL with nano Electrospray Ionization (ESI) from the Analytical Research and Services of the University of Bern.

Absorption spectra were measured on an Agilent Cary 100 spectrophotometer using quartz cuvettes with an optical path of 1cm. Fluorescence spectra were recorded on a Cary Eclipse fluorescence spectrophotometer setting the excitation and emission slits to 5 nm. The supramolecular polymer formation of **N-Phe$_3$** (vesicles) was performed via thermal disassembly and reassembly process. **N-Phe$_3$** in ethanol was added to a solution of 10 mM sodium acetate buffer (pH 4.7) and 10 vol% ethanol. The sample was heated to 70 °C to fully disassemble the **N-Phe$_3$** and then cooled to 20 °C with a controlled rate of 0.33 °C/min in an Eppendorf Thermomixer Compact to form the **N-Phe$_3$** vesicles. The formed vesicles were stable for at least 24h. The formation of **Py$_3$**-nanosheets was achieved in 10 mM sodium phosphate buffer (pH 7.1), 10 mM sodium chloride and 10 vol% ethanol with a controlled cooling rate of 0.5 °C/min from 70°C to 20°C in a Cary 100 spectrophotometer equipped with a Peltier thermostat.

Atomic force microscopy (AFM) measurements were performed on a Nanosurf FlexAFM instrument in tapping mode under ambient conditions. Tap190-Al-G cantilevers from Budget-Sensors were used with a resonant frequency of 190kHz, a force constant of 48N/m and a tip radius of 10 nm. Mica sheets (Glimmer “V1”, 20mm x 20mm, G250-7, Plano GmbH) were used as substrates. The graphical illustration and evaluation of the AFM measurements was done with the softwares Nanosurf C300 and SPIP. The mica sheets were APTES-modified according to published procedures.[2] For every sample preparation, 30µl of the sample solution was pipetted onto the mica sheet. After 10 minutes of adsorption time, the solution was sucked with a KIMTECH^{Science*} precision wipe and the mica was rinsed with Milli-Q water (1ml), then dried under an argon stream.

For the electrostatic layer assembly, the two molecules **N-Phe$_3$** and **Py$_3$** had to be preassembled as previously described. **Py$_3$**-sheets were adsorbed on APTES-modified mica, the mica was washed and dried as previously described, and afterwards the second layer, positively charged **N-Phe$_3$**-vesicles, was adsorbed on top and treated like before.

Transmission electron microscopy (TEM) was performed on a Tecnai Spirit instrument with an operating voltage of 80kV and with either an Olympus-SIS Veleta CCD camera or FEI Eagle CCD camera. The **N-Phe$_3$** was self-assembled as previously described, and a carbon-coated copper grid (300 Mesh, Agar Scientific) was used as a substrate. The samples were prepared as followed: 5µl of the supramolecular polymer was dropped onto the grid, waited for 10min, and the solution was blotted. Afterwards the grid was washed by dipping into 20µl of Milli-Q water and blotting two times. The last step was the staining of the sample with a 0.5% aqueous uranyl-acetate solution. This was done according to the washing procedure: the sample was dipped twice into 20µl of the uranyl-acetate solution (0.5%).

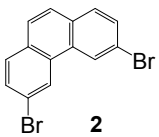
DLS measurements were carried out on a Zetasizer Nano instrument (Malvern Instruments) by using the standard operation procedure for particle size determination. Pre-washed plastic cuvettes were used for the measurements. The equilibration time at 70 °C was 5 minutes, before cooling to 20 °C.

The zeta potential and the size distribution measurements were determined by nanoparticle tracking analysis (NTA) with a ZetaView (software version 8.05.05 SP2, ParticleMetrix, Inning am Ammersee, Germany) equipped with a 488 nm laser, zeta potential and temperature control units. Measurements were performed at 20 °C, a camera sensitivity of 85, and 100 1/ms shutter value.

3 Organic synthesis

3.1 N-Phe$_3$

3,6-Dibromophenanthrene (2)



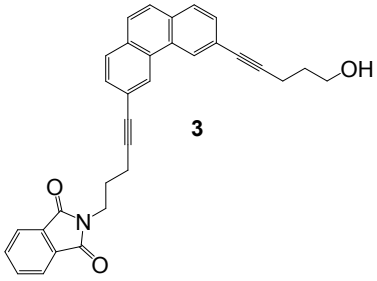
2

The commercially available 4,4’-dibromo-trans-stilbene (**1**) (2.5036 g, 7.41 mmol) and Iodine (0.3638 g, 1.43 mmol) was dissolved in toluene (4 l). The solution was irradiated with a mercury medium pressure UV lamp for 70 hours while air was bubbled through. The reaction was monitored by ^{1}H NMR. Water (1 l) and an excess of $Na_2S_2O_3$ were added to remove the iodine (color change from pink to beige). The organic phase was evaporated under reduced pressure. The obtained yellow solid was dissolved in boiling DCM (99 ml), methanol (60 ml) was added, and the solution was kept for 2 days in

the fridge. The white crystals were filtrated off and washed with cold DCM (7 ml). The filtrate was evaporated and recrystallized again. The combined fractions of compound **2** were obtained in 70% yield (1.7460 g). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.69 (d, J = 1.6 Hz, 2H), 7.79 – 7.65 (m, 6H).

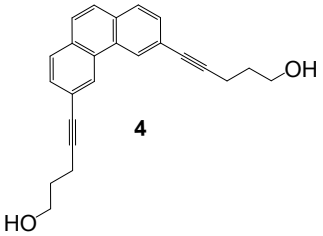
2-(5-(6-(5-hydroxypent-1-yn-1-yl)phenanthren-3-yl)pent-4-yn-1-yl)isoindoline-1,3-dione (3) and

5,5'-(phenanthrene-3,6-diyl)bis(pent-4-yn-1-ol) (4)



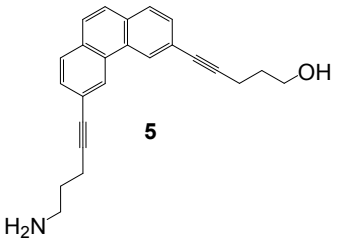
3

To a degassed solution of 3,6-Dibromophenanthrene **2** (1.0016 g, 2.98 mmol) in dry THF (33 ml) and Et_3N (16.5 ml) under an argon atmosphere, $Pd[Ph_3P]_2Cl_2$ (116.7 mg, 0.166 mmol), CuI (51.9 mg, 0.273 mmol), 4-Pentynyl-phthalimide (635.9 mg, 2.98 mmol) and 4-Pentyn-1-ol (275.5 µl, 2.98 mmol) was added. The black solution was refluxed overnight. The mixture was filtrated, the filtrate was washed with citric acid (10%) and saturated $NaHCO_3$ solution. The solution was dried over Na_2SO_4 and concentrated *in vacuo*. The crude products **3** and **4** were separated by flash column chromatography on silica gel (hexane/EtOAc 3:1). Compound **3** was isolated as an orange-yellowish solid (437.1 mg, 31%). Compound **4** was isolated as an orange solid (164.7 mg, 16%). **3**: R_f = 0.24 (hexane/EtOAc 1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.51 (s, 1H), 7.84 – 7.68 (m, 4H), 7.65 (s, 2H), 7.62 –7.41 (m, 4H), 3.98 – 3.86 (m, 4H), 2.71 – 2.54 (m, 4H), 2.10 (p, J = 6.9 Hz, 2H), 1.96 (p, J = 6.6 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.68, 133.96, 132.29, 131.42, 129.71, 128.43, 127.06, 126.42, 123.30, 122.12, 90.34, 81.91, 61.99, 37.69, 31.56, 27.40, 17.68, 16.30. HRMS-NSI (*m/z*): $[M+H]^+$ calcd for $C_{32}H_{26}NO_3$: 472.1907, found: 472.1895. **4**: R_f = 0.06 (hexane/EtOAc 1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.69 (s, 2H), 7.77 (d, J = 8.2 Hz, 2H), 7.67 (s, 2H), 7.63 – 7.53 (m, 2H), 3.90 (t, J = 6.2 Hz, 4H), 2.64 (t, J = 6.9 Hz, 4H), 1.94 (p, J = 6.6 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.54, 129.78, 129.61, 128.62, 127.15, 126.28, 122.16, 90.33, 81.83, 62.04, 31.57, 16.30. HRMS-NSI (*m/z*): $[M+H]^+$ calcd for $C_{24}H_{23}O_2$: 343.1693, found: 343.1703.



4

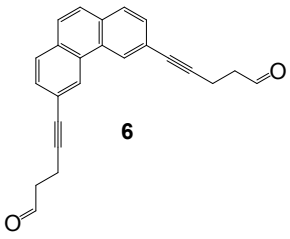
5-(6-(5-aminopent-1-yn-1-yl)phenanthren-3-yl)pent-4-yn-1-ol (5)



5

A solution of compound **3** (212.8 mg, 0.451 mmol) and hydrazine-monohydrate (0.18 ml, 3.610 mmol) in THF (9 ml) was stirred at 40 °C, under argon atmosphere overnight. The grey precipitation was filtrated off and the filtrate was diluted with DCM (100 ml). The filtrate was washed two times with 2M K_2CO_3 (2x 100 ml). The organic phase was dried over K_2CO_3 and concentrated *in vacuo*. Compound **5** was gained as a yellow sticky solid (149.7 mg, 97%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.69 (s, 2H), 7.77 (d, J = 8.2 Hz, 2H), 7.66 (s, 2H), 7.62 – 7.54 (m, 2H), 3.89 (t, J = 6.2 Hz, 2H), 2.94 (t, J = 6.9 Hz, 2H), 2.60 (dt, J = 18.5, 6.9 Hz, 4H), 1.94 (p, J = 6.7 Hz, 2H), 1.82 (p, J = 6.9 Hz, 2H).^{13}C NMR (75 MHz, $CDCl_3$) δ 131.35, 129.59, 129.46, 128.46, 126.96, 126.18, 122.02, 90.42, 81.68, 61.73, 41.38, 32.48, 31.45, 17.06, 16.16. HRMS-NSI (*m/z*): $[M+H]^+$ calcd for $C_{24}H_{24}NO$: 342.1852, found: 342.1849.

5,5'-(phenanthrene-3,6-diyl)bis(pent-4-ynal) (6)

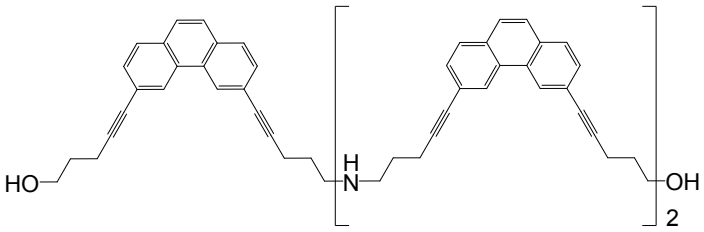


6

The procedure was carried out analog to reference.[3] Dess-Martin Periodinane (DMP) (817.2 mg, 1.926 mmol) was dissolved in DCM (9 ml) and placed under argon. Compound **4** (299.8 mg, 0.876 mmol) was dissolved in DCM (9 ml) and was added to the DMP solution. The reaction mixture was stirred at RT for 1 hour. The reaction mixture was diluted with DCM (50 ml) and washed with sat. aq. $NaHCO_3$ solution containing 12.5 g $Na_2S_2O_3$ (50 ml), sat. aq. $NaHCO_3$ soution (50 ml) and water (50 ml). The organic phase was dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (hexane/EtOAc 3:1). The product was gained as a white yellowish fluffy solid (120.8 mg, 41%). R_f = 0.3 (hexane/EtOAc 2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.92 (s, 2H), 8.69 (s, 2H), 7.78 (d, J = 8.2 Hz, 2H), 7.68 (s, 2H), 7.62 – 7.52 (m, 2H), 2.88 – 2.80 (m, 8H). ^{13}C NMR (75

MHz, $CDCl_3$) δ 200.99, 132.09, 130.20, 130.01, 129.08, 127.68, 126.78, 122.24, 89.16, 82.53, 43.24, 13.41. HRMS-NSI (*m/z*): $[M+Na]^+$ calcd for $C_{24}H_{18}O_2Na$: 361.1199, found: 361.1198.

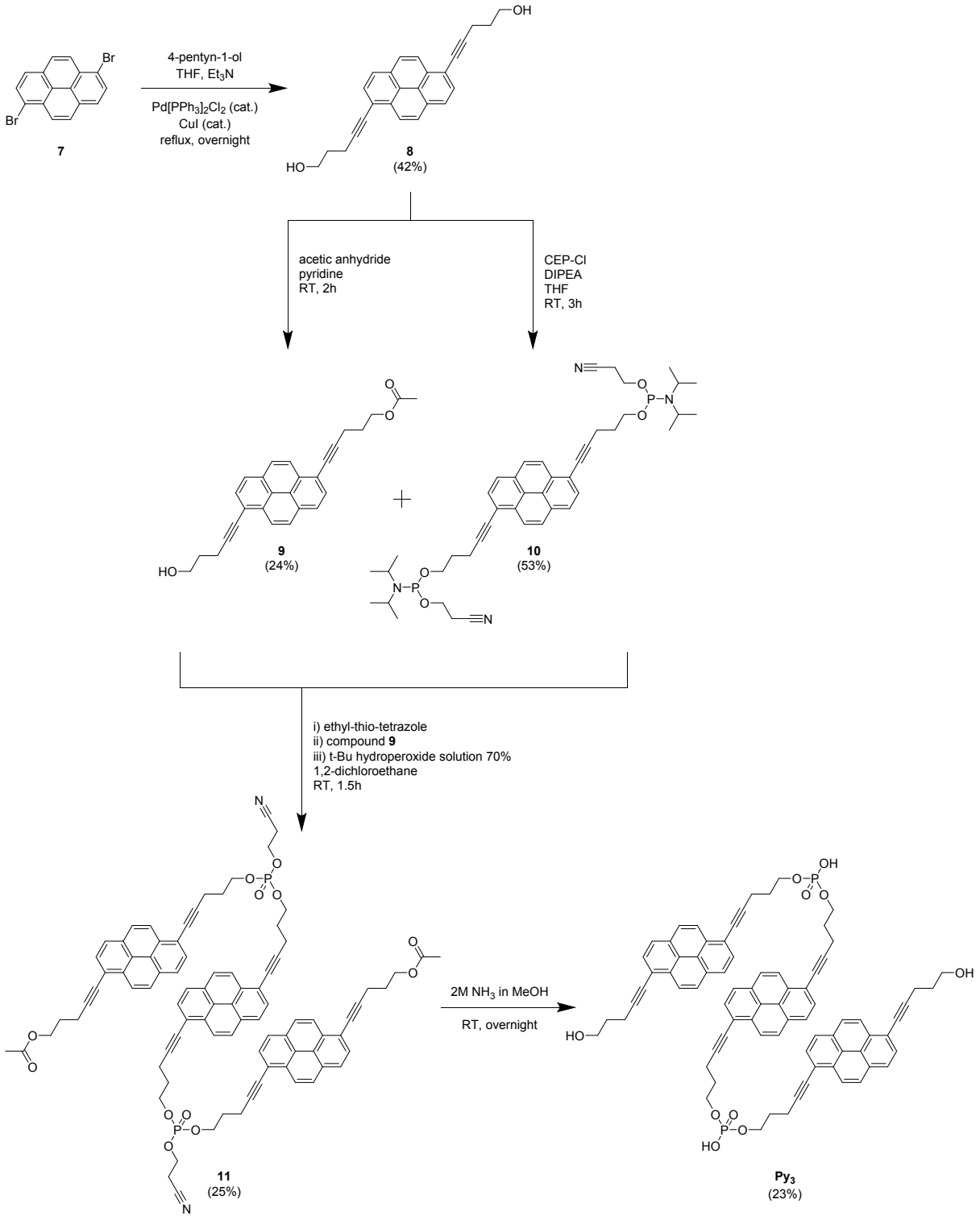
5,5'-((((phenanthrene-3,6-diylbis(pent-4-yne-5,1-diyl))bis(azanediyl))bis(pent-1-yne-5,1-diyl))bis(phenanthrene-6,3-diyl))bis(pent-4-yn-1-ol) (N-Phe$_3$)



N-Phe$_3$

The procedure was carried out analog to reference.[4] A solution of **5** (20.2 mg, 0.0591 mmol) and $Na(OAc)_3BH$ (25.5 mg, 0.12 mmol) in $CHCl_3$ (6 ml) was placed under argon and a solution of **6** (10.0 mg, 0.0296 mmol) in $CHCl_3$ (3 ml) was added dropwise. The reaction was stirred overnight. The reaction mixture was diluted with $CHCl_3$ (15 ml) and washed twice with 2 M K_2CO_3 solution. The $CHCl_3$-phase was dried over K_2CO_3 and concentrated *in vacuo*. The crude product was purified by preparative TLC (DCM/MeOH 95:5 + 1% Et_3N) and yielded **N-Phe$_3$** as a white-yellowish solid (22.8 mg, 78%). R_f = 0.22 (DCM/MeOH 95:5+1% Et_3N). HRMS-NSI (*m/z*) $[M+H]^+$ calcd for $C_{72}H_{65}N_2O_2$: 989.5041, found: 989.5042.

3.2 Py_3



Scheme S1. The synthesis of the 1,6-dipentynyl linked pyrene trimer with phosphodiester-bridges (**Py_3**).

5,5'-(Pyrene-1,6-diyl)bis(pent-4-yn-1-ol) (8)

Compound **8** was synthesized according to literature.[6] 1,6-Dibromopyrene (**7**) (1.0201 g, 2.833 mmol) was dissolved in anhydrous THF (23 ml) and degassed Et_3N (14 ml) under an argon atmosphere and heated to 84 °C. 4-Pentyn-1-ol (1 ml, 10.8 mmol) was added, followed by the catalysts $Pd[PPh_3]_2Cl_2$ (52 mg, 0.074 mmol) and CuI (10 mg, 0.053 mmol). The reaction mixture was refluxed at 84 °C overnight. TLC (DCM/MeOH 92:8) showed the

disappearance of starting material **7**. The reaction mixture was cooled to RT, before it was diluted with DCM (100ml), and filtrated through Celite 503. The filtrate was washed once with 10% citric acid (100ml), once with aq. sat. $NaHCO_3$ (100ml), dried over Na_2SO_4, filtrated, and concentrated under reduced pressure. The residue was purified by a flash column chromatography on silica gel (DCM/toluene/MeOH 88:10:2). Compound **8** could be isolated as a pure yellow compound (437.4 mg, 42%). R_f = 0.23 (DCM/MeOH 97:3). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.52 (d, J = 9.1 Hz, 2H), 8.13 – 8.02 (m, 6H), 3.96 (t, J = 6.2 Hz, 4H), 2.79 (t, J = 7.0 Hz, 4H), 2.04 (p, J = 6.6 Hz, 4H).

5-(6-(5-Hydroxypent-1-yn-1-yl)pyren-1-yl)pent-4-yn-1-yl acetate (9)

Compound **8** (152.6 mg, 0.416 mmol) was dissolved in pyridine (4.2 ml) under argon. A 2M solution of acetic anhydride (0.2 ml, 0.416 mmol) in pyridine was added dropwise over ten minutes to the dissolved compound **8**. The reaction mixture was stirred at RT for 2 hours until TLC (hexane/EtOAc 3:2) showed mainly the mono-acetylated product (**9**) and some unreacted starting material **8**. The reaction mixture was diluted with DCM (10ml) and washed once with aq. 0.5 M HCl (10ml), once with aq. sat. $NaHCO_3$ (10ml) and once with brine (10ml). The organic phase was dried over $MgSO_4$, filtrated, and the solvent removed under reduced pressure. The residue was purified by a flash column chromatography on silica gel (hexane/EtOAc 3:2). Compound **9** could have been isolated as a pure, yellow solid (41.1 mg, 24%). R_f = 0.55 (hexane/EtOAc 1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.53 (d, J = 11.1 Hz, 2H), 8.15 - 8.03 (m, 6H), 4.36 (t, J = 6.3 Hz, 2H), 3.96 (t, J = 6.2 Hz, 2H), 2.85 - 2.71 (m, 4H), 2.16 - 1.98 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.11, 130.86, 130.82, 130.04, 128.05, 128.02, 126.11, 126.07, 124.99, 124.97, 124.31, 119.07, 118.94, 95.65, 94.86, 63.49, 62.05, 31.79, 28.20, 21.15, 16.90, 16.65. HRMS-NSI (*m/z*): $[M]^+$ calcd for $C_{28}H_{24}O_3$: 408.1720, found: 408.1701.

Bis(2-cyanoethyl) (pyrene-1,6-diylbis(pent-4-yne-5,1-diyl)) bis(diisopropylphosphoramidite) (10)

Compound **8** (100.3 mg, 0.274 mmol) was dissolved in anhydrous THF (6 ml) and DIPEA (0.5 ml, 2.93 mmol). CEP-Cl (210 mg, 0.887 mmol) was added dropwise at RT and the reaction mixture stirred for 3 hours. TLC (hexane/EtOAc 7:3 + 1% Et_3N) showed the disappearance of starting material. The reaction mixture was concentrated under reduced pressure. The resultant yellow-greenish foam was purified by a short flash column chromatography on silica gel (hexane/EtOAc 8:2 + 1% Et_3N). Product **10** could have been isolated as a yellow-greenish oil (112.0 mg, 53%). R_f = 0.81 (hexane/EtOAc 6:4 + 1% Et_3N). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.55 (d, J = 9.1 Hz, 2H), 8.15 – 7.95 (m, 6H), 4.04 – 3.76 (m, 8H), 3.74 – 3.56 (m, 4H), 2.78 (t, J = 7.0 Hz, 4H), 2.65 (t, J = 6.5 Hz, 4H), 2.14 – 2.01 (m, 4H), 1.26 – 1.18 (m, 24H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.08, 130.76, 130.00, 127.94, 126.14, 124.92, 124.30, 119.17, 117.75, 95.67, 80.05, 62.57, 62.34, 58.62, 58.36, 43.57, 43.27, 43.11, 30.67, 30.57, 24.81, 24.72, 20.55, 20.46, 16.74. ^{31}P NMR (121 MHz, $CDCl_3$) δ 147.84. HRMS-NSI (*m/z*): $[M+H]^+$ calcd for $C_{44}H_{57}O_4N_4P_2$: 767.3850, found: 767.3816.

Protected 1,6-dipentynyl substituted pyrene-trimer (11)

A solution of 5-(ethylthio)-1*H*-tetrazole (9.9 mg, 0.076 mmol) in DCE (0.25 ml) was added under argon atmosphere to a solution of compound **10** (15 mg, 0.02 mmol) in DCE (0.14 ml). Compound **9** (25.1 mg, 0.061 mmol) was dissolved in DCE (0.48 ml) and added to the activated compound **10**. The reaction was stirred at room temperature for one hour. *Tert*-Butyl hydroperoxide solution (70%, 16.2 µl, 0.117 mmol) was added and further stirred for 10 minutes. The reaction mixture was diluted with chloroform (15 ml) and washed once with aq. sat. $NaHCO_3$ (15 ml) and once with brine (15 ml). The organic layer was dried over $MgSO_4$, filtrated, and concentrated under reduced pressure. The residue was purified by a preparative TLC (DCM/toluene/MeOH 86:10:4). Compound **11** was purely isolated (6.9 mg, 25%). R_f = 0.43 (DCM/toluene/MeOH 86:10:4). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.54 – 8.30 (m, 6H), 8.14 – 7.86 (m, 18H), 4.51 – 4.25 (m, 16H), 2.91 – 2.66 (m, 16H), 2.22 – 2.04 (m, 18H). ^{31}P NMR (121 MHz, $CDCl_3$) δ -1.37. HRMS-NSI (*m/z*): $[M]^+$ calcd for $C_{88}H_{74}O_{12}N_2P_2$: 1412.4712, found: 1412.4648.

1,6-dipentynyl substituted pyrene trimer (Py_3)

Compound **11** (6.9 mg, 0.0049 mmol) was dissolved in a solution of 2 mol/l NH_3 in methanol (5 ml) and stirred at RT overnight. The sample was lyophilized, the residue was suspended in MeOH (1 ml) and lyophilized again and yielded the product **Py_3** (6.0 mg, quant.). HRMS-NSI (*m/z*): $[M-H]^-$ calcd for $C_{78}H_{64}O_{10}P_2$: 1222.3975, found: 1222.4007.

4 NMR spectra

4.1 N-Phe$_3$

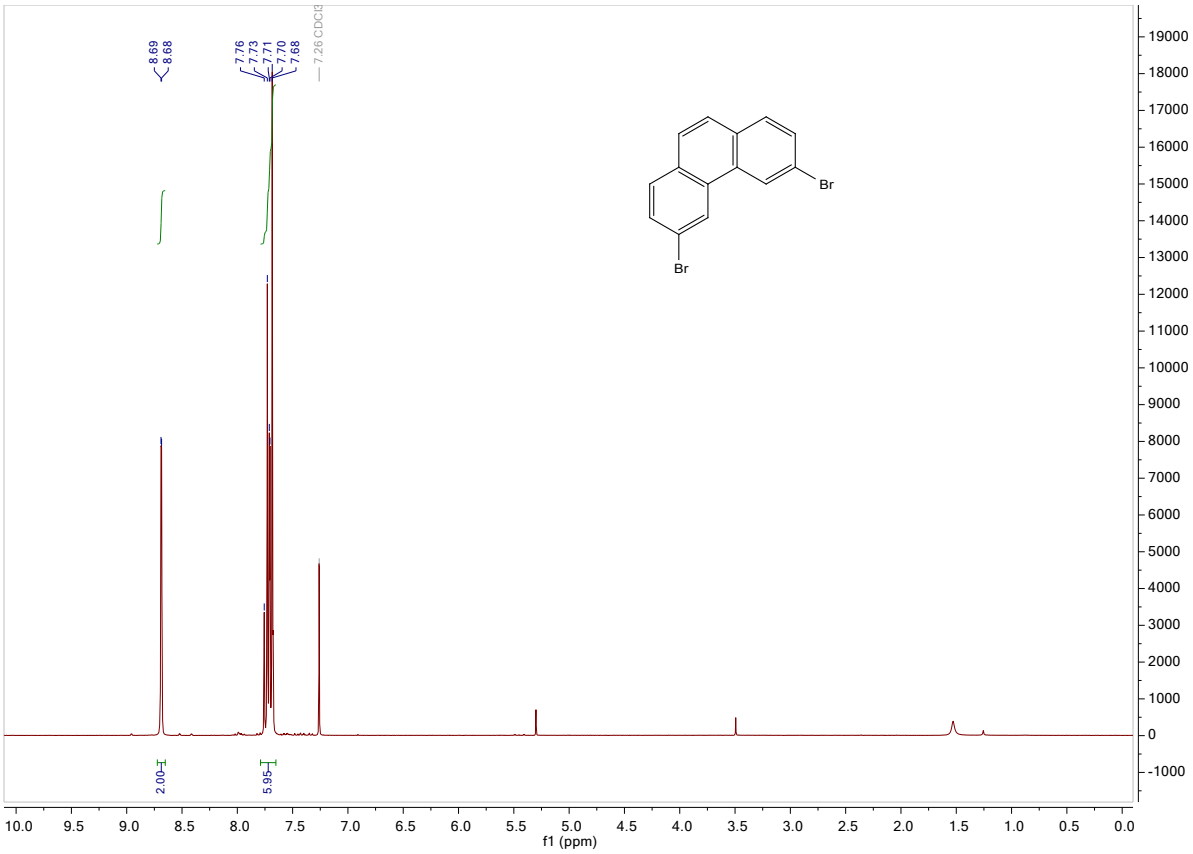


Figure S1. ^{1}H NMR of compound **2** in $CDCl_3$.

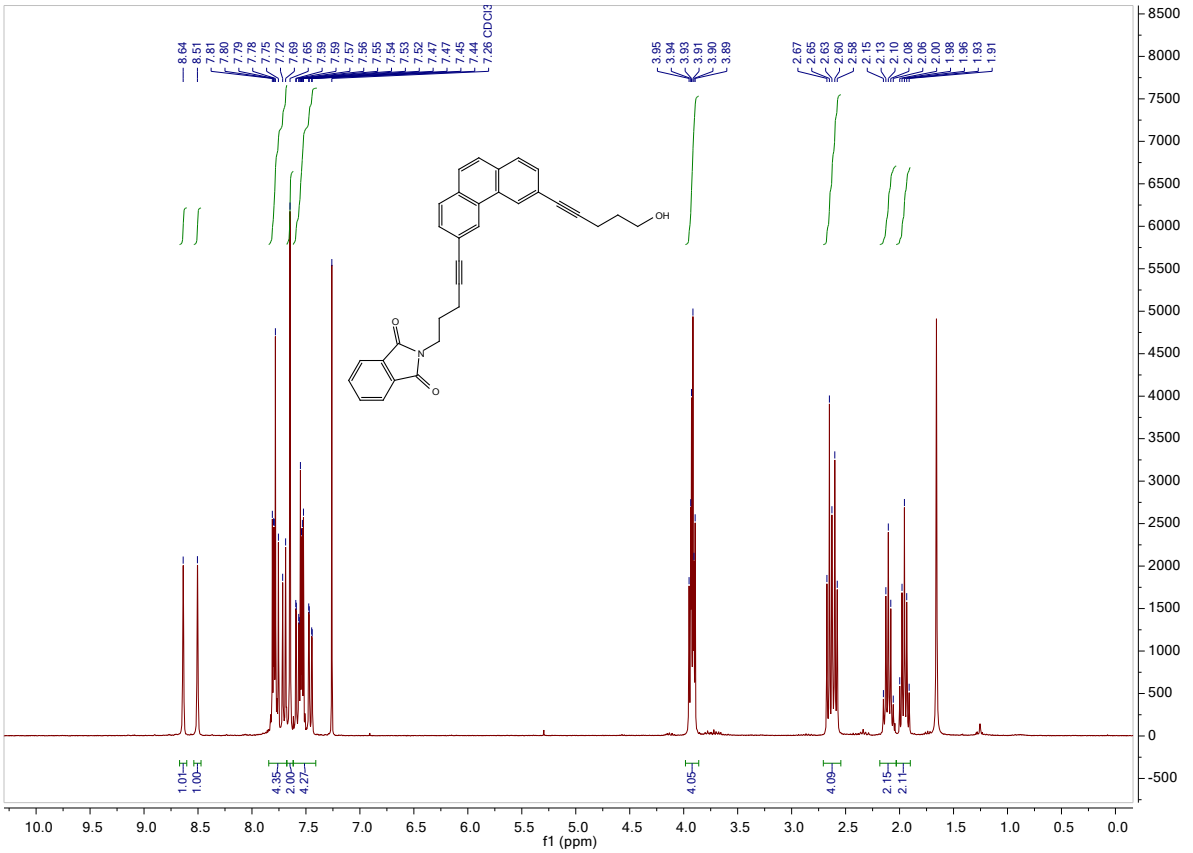


Figure S2. ^{1}H NMR of compound **3** in $CDCl_3$.

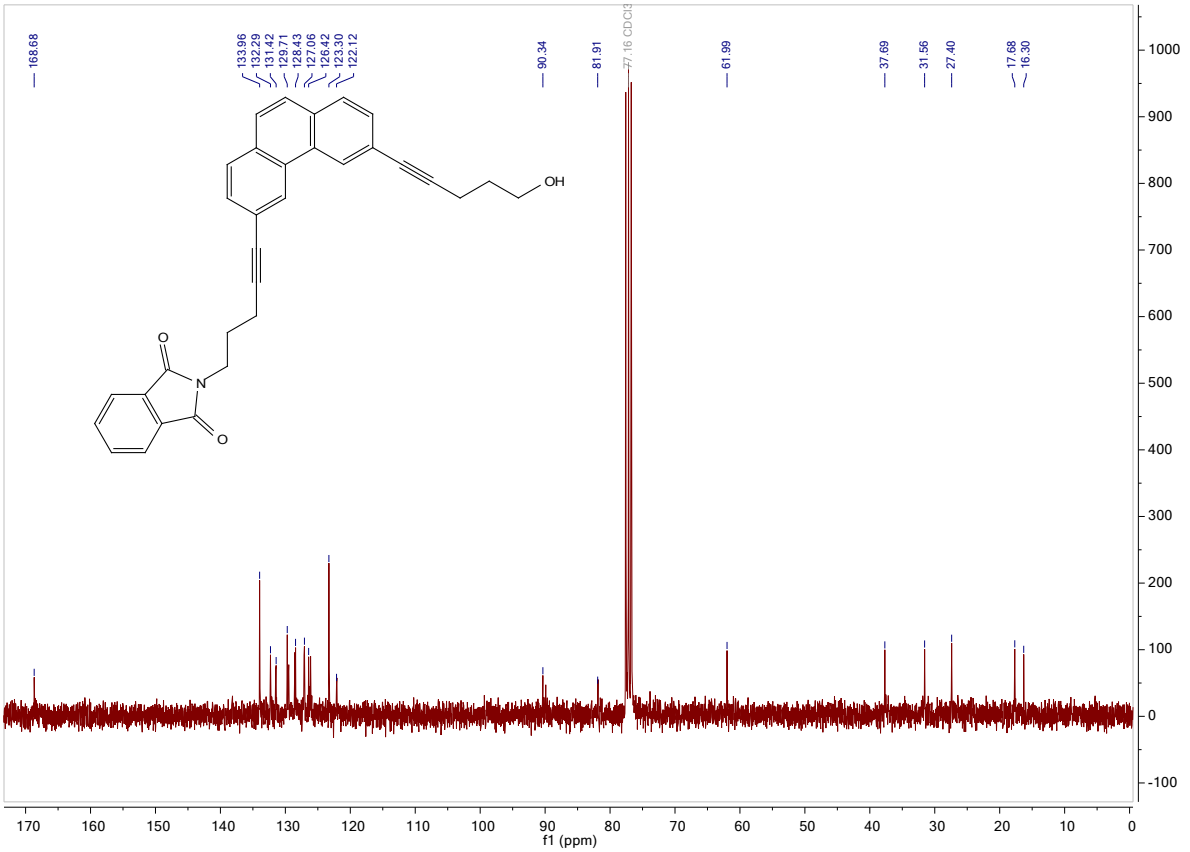


Figure S3. ^{13}C NMR of compound **3** in $CDCl_3$.

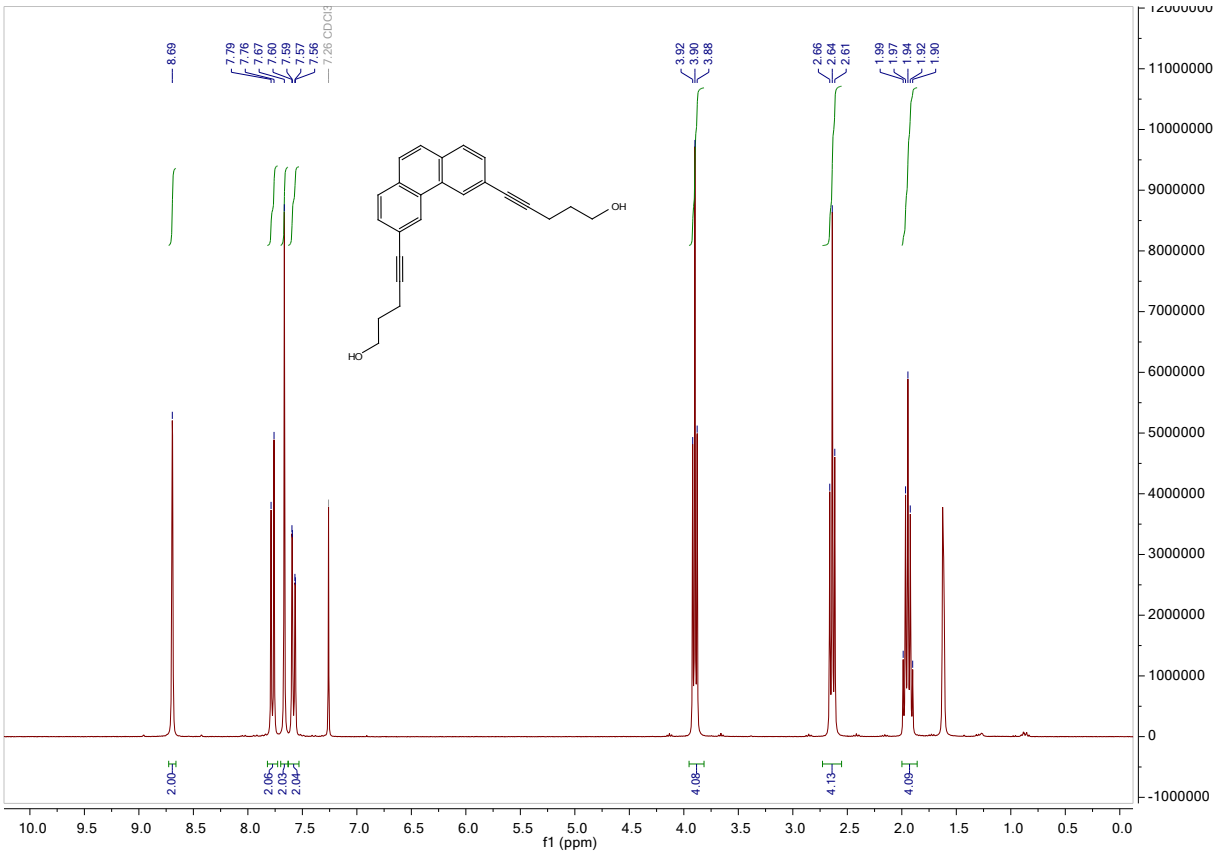


Figure S4. ^{1}H NMR of compound **4** in $CDCl_3$.

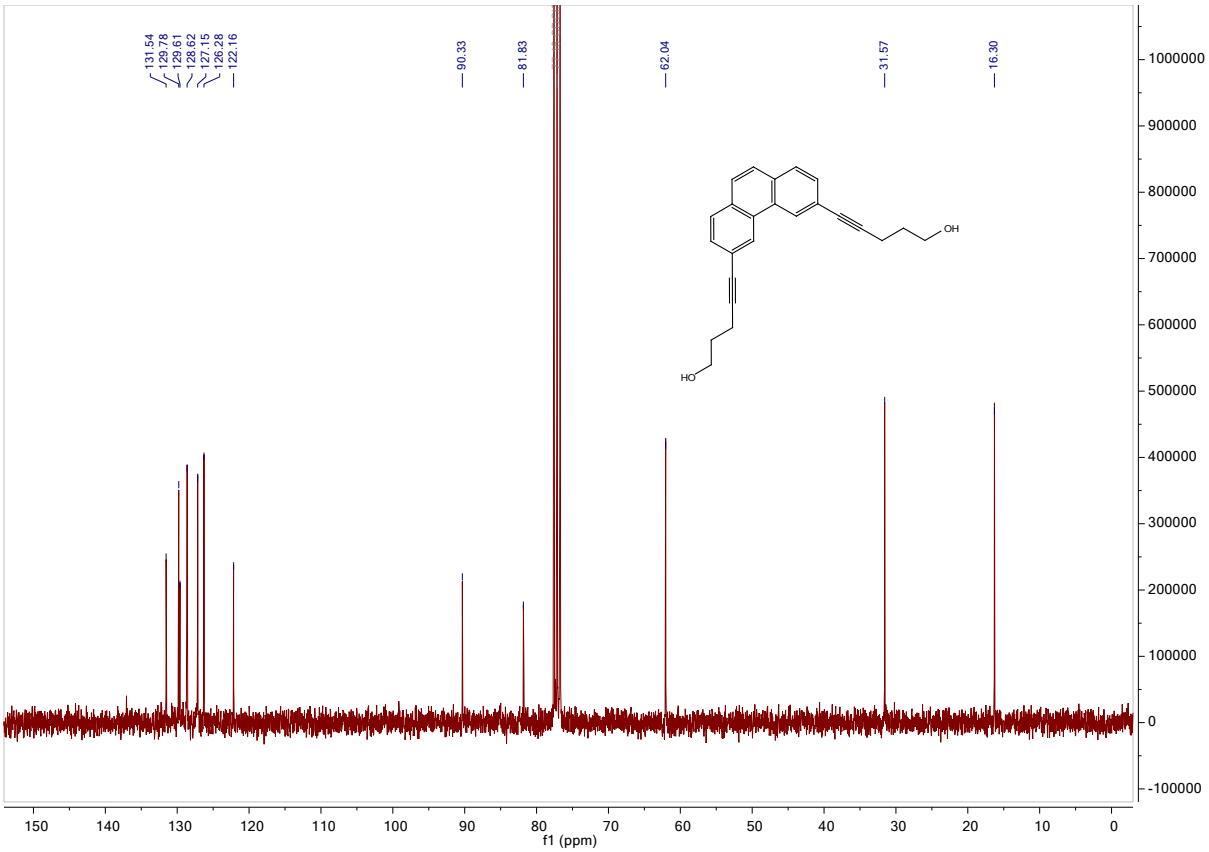


Figure S5. ^{13}C NMR of compound **4** in $CDCl_3$.

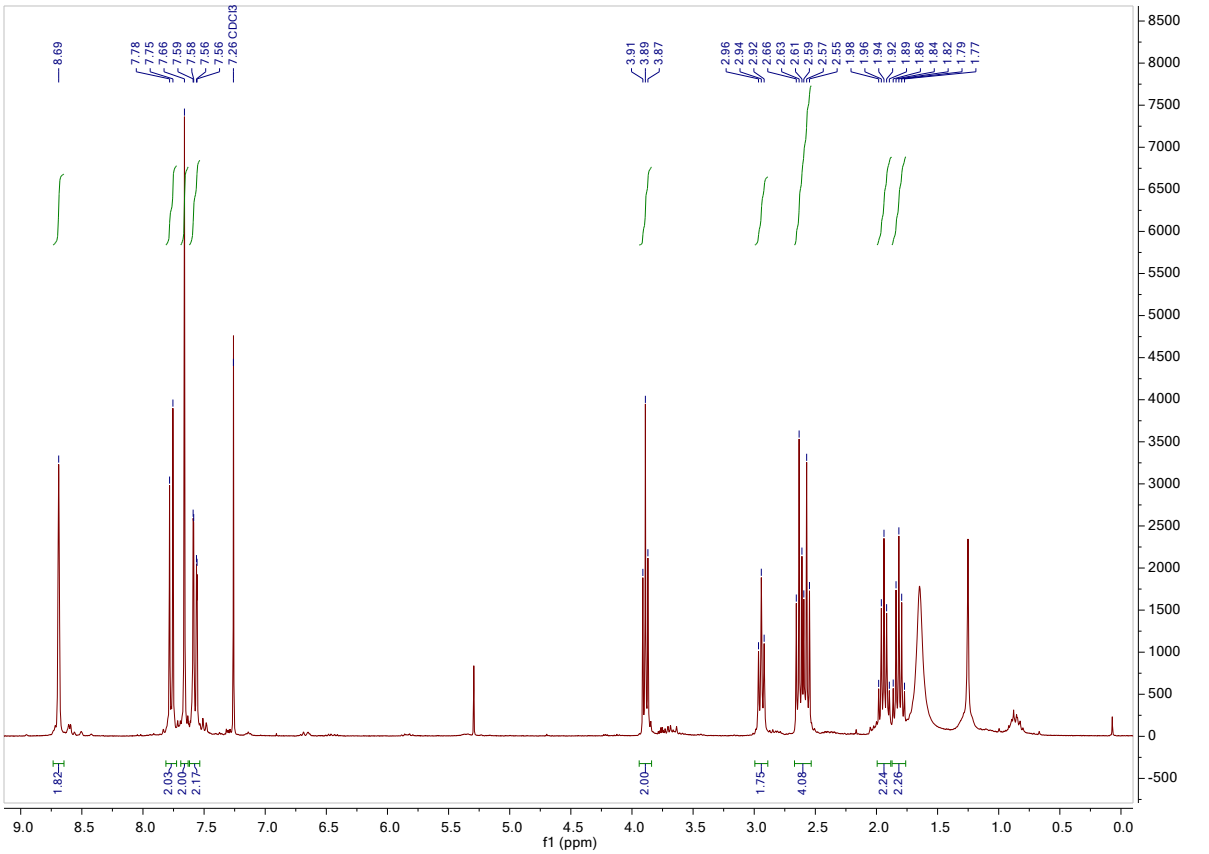


Figure S6. ^{1}H NMR of compound **5** in $CDCl_3$.

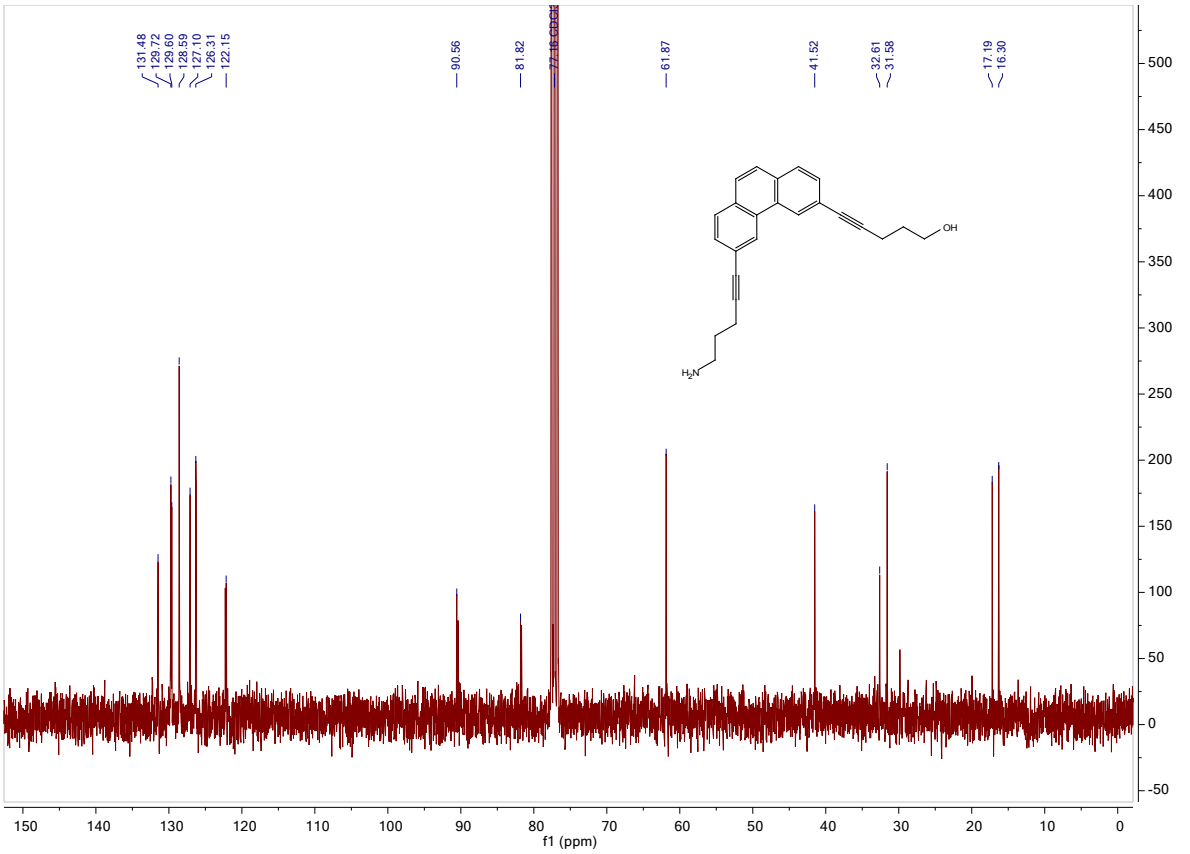


Figure S7. ^{13}C NMR of compound **5** in $CDCl_3$.

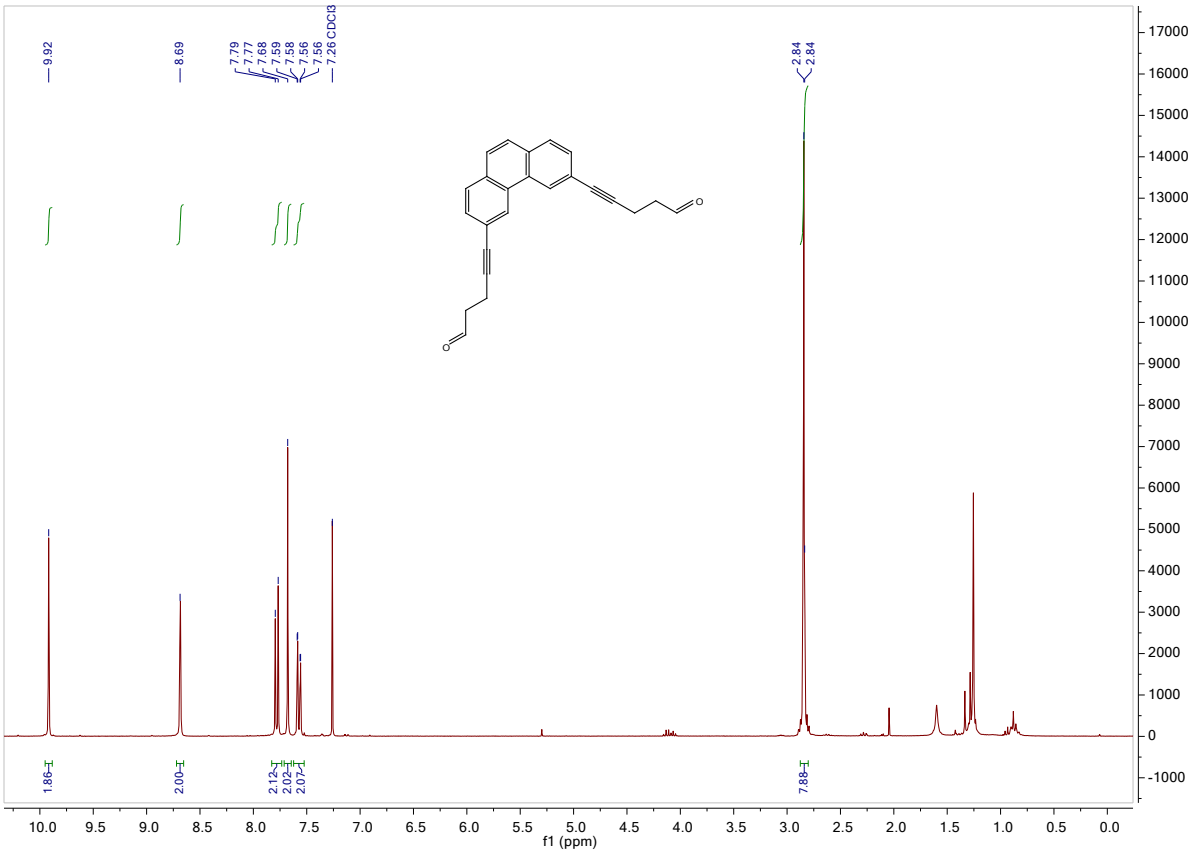


Figure S8. ^{1}H NMR of compound **6** in $CDCl_3$.

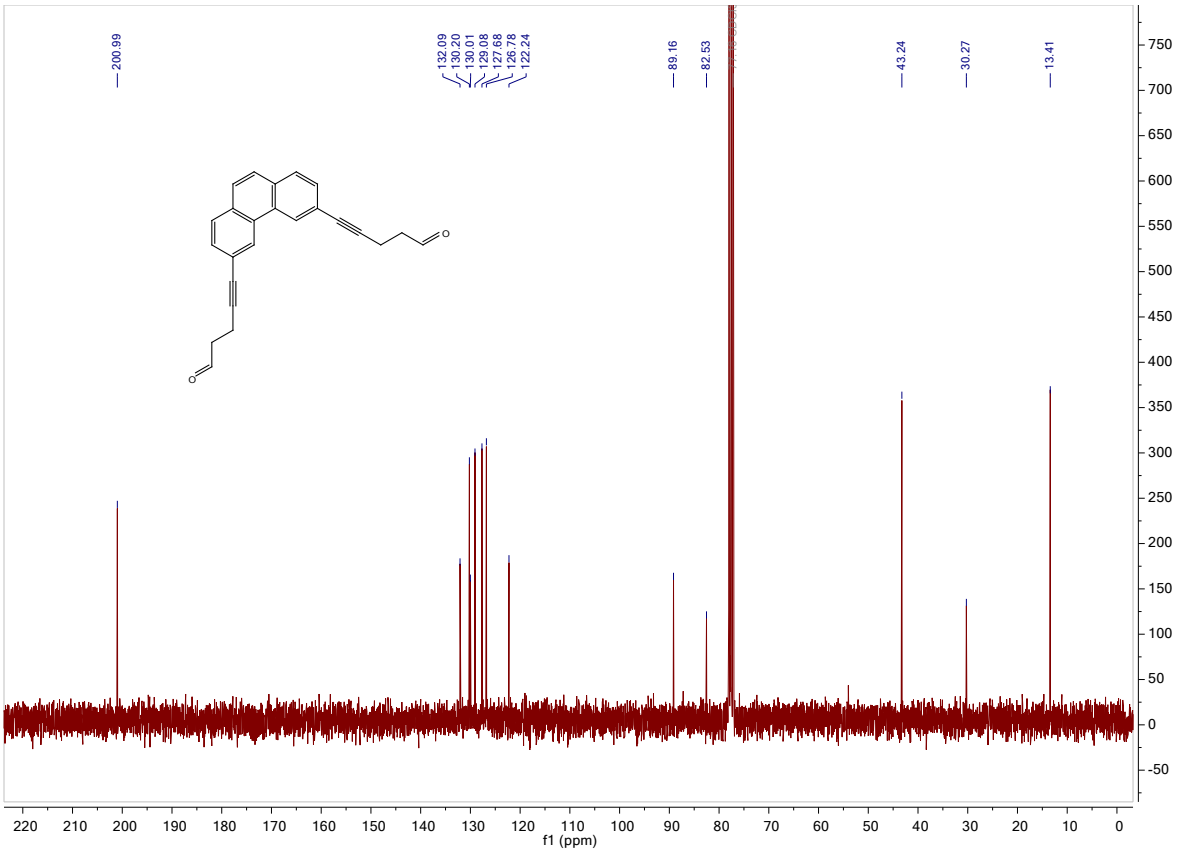


Figure S9. ^{13}C NMR of compound **6** in $CDCl_3$.

4.2 Py_3

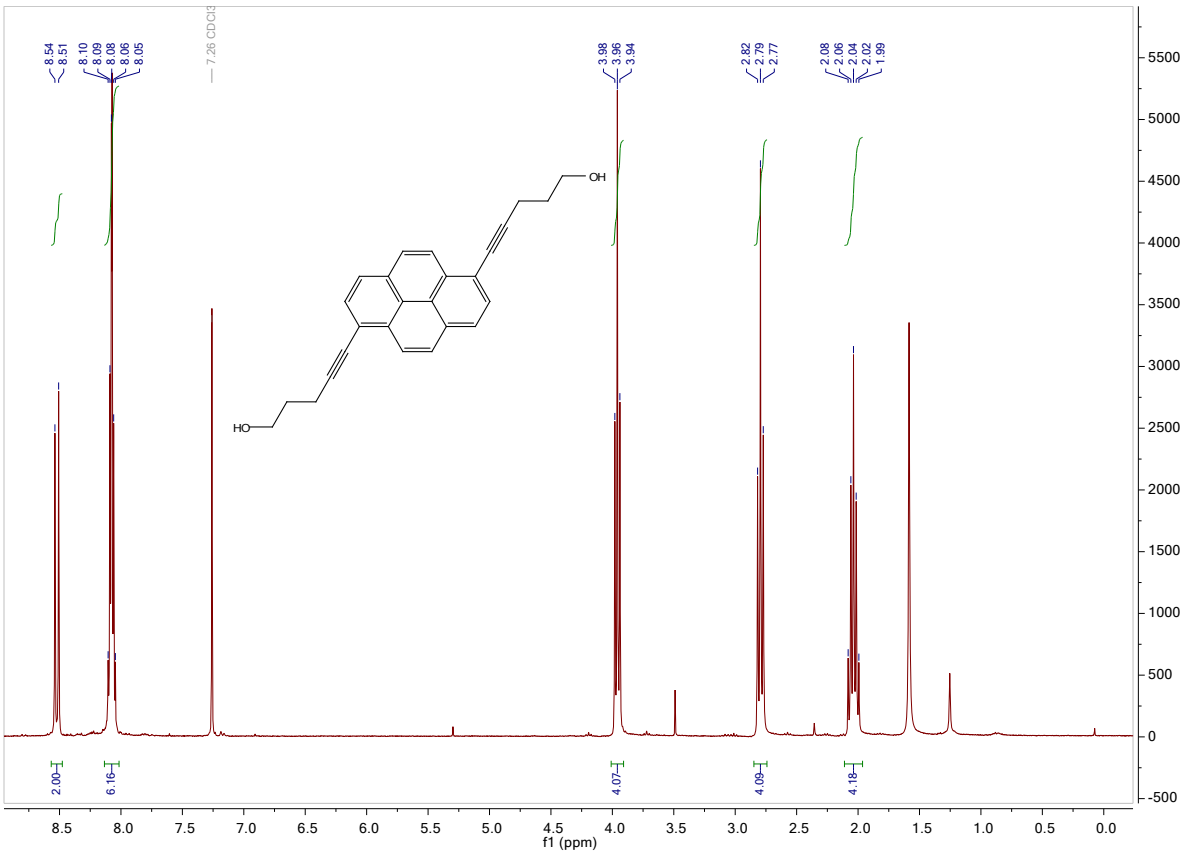


Figure S10. ^{1}H of compound **8** in $CDCl_3$.

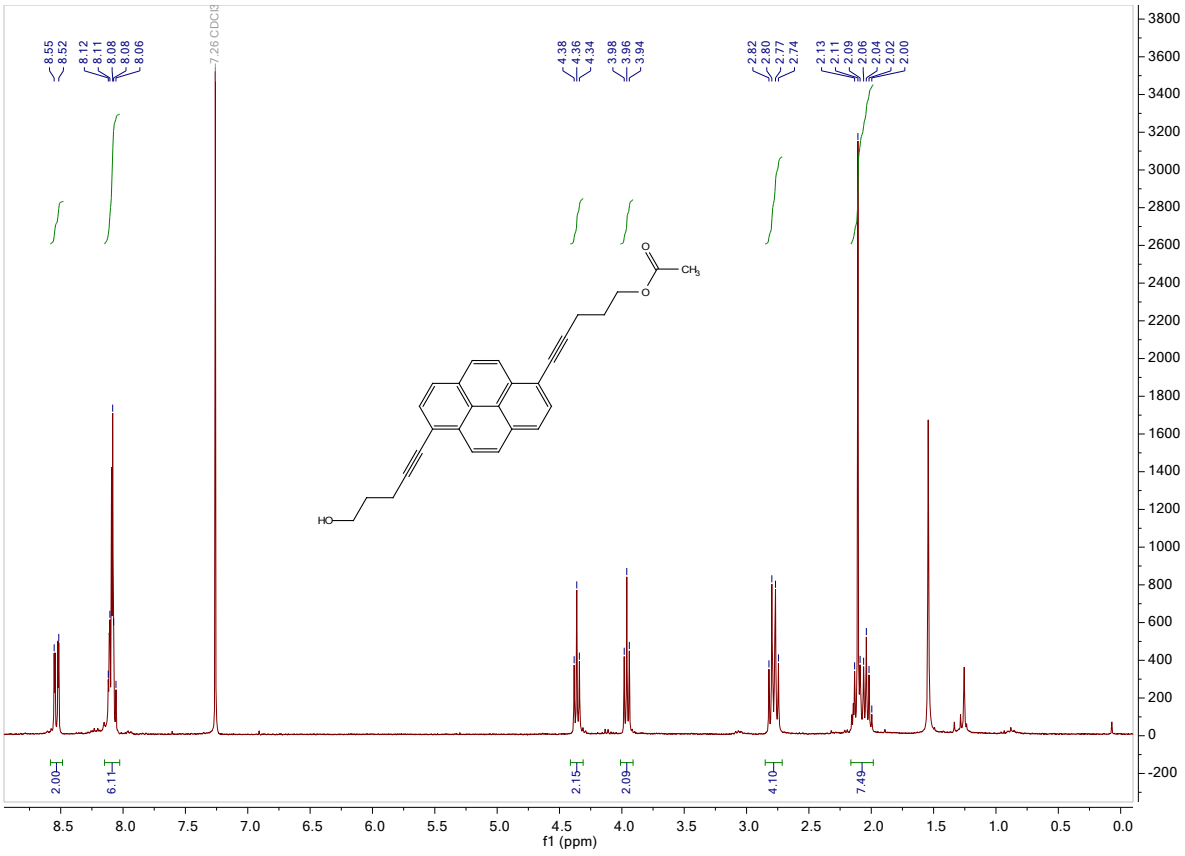


Figure S11. ^{1}H NMR of compound **9** in $CDCl_3$.

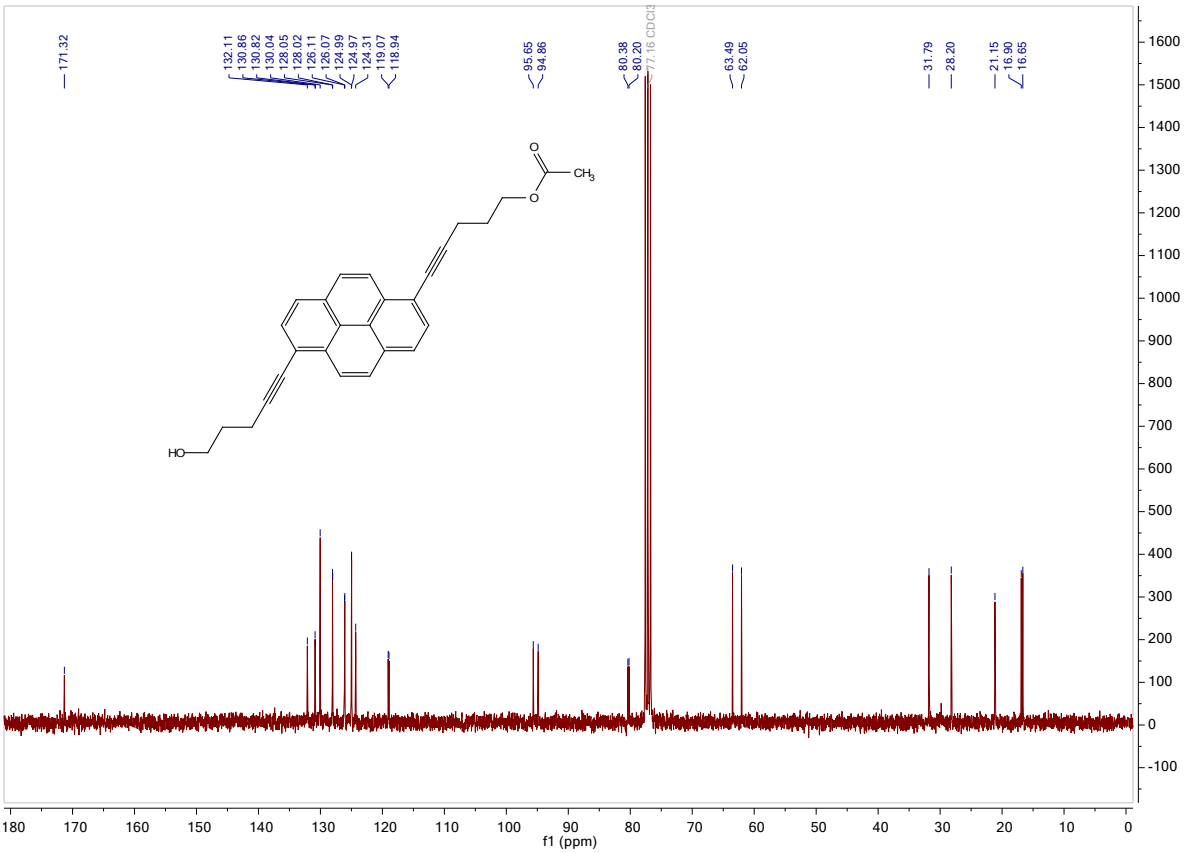


Figure S12. ^{13}C NMR of compound **9** in $CDCl_3$.

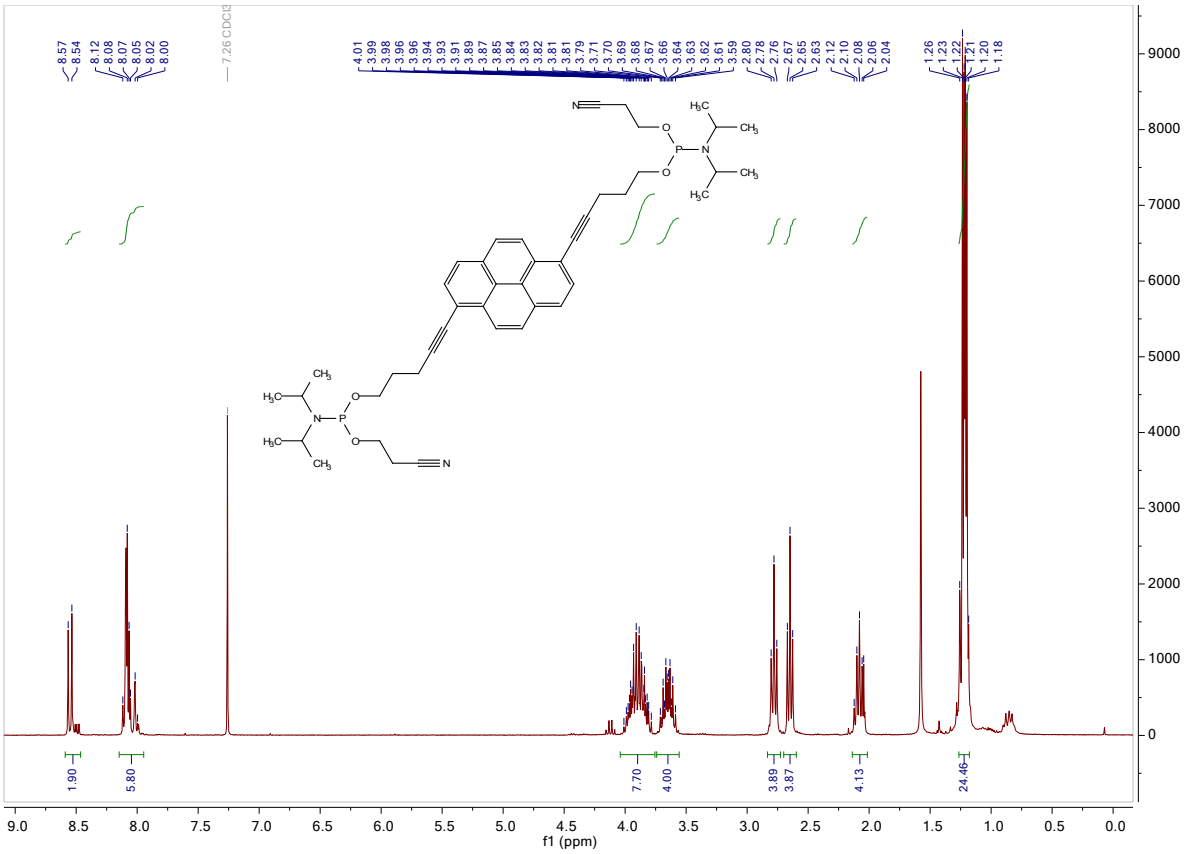


Figure S13. ^{1}H NMR of compound **10** in $CDCl_3$.

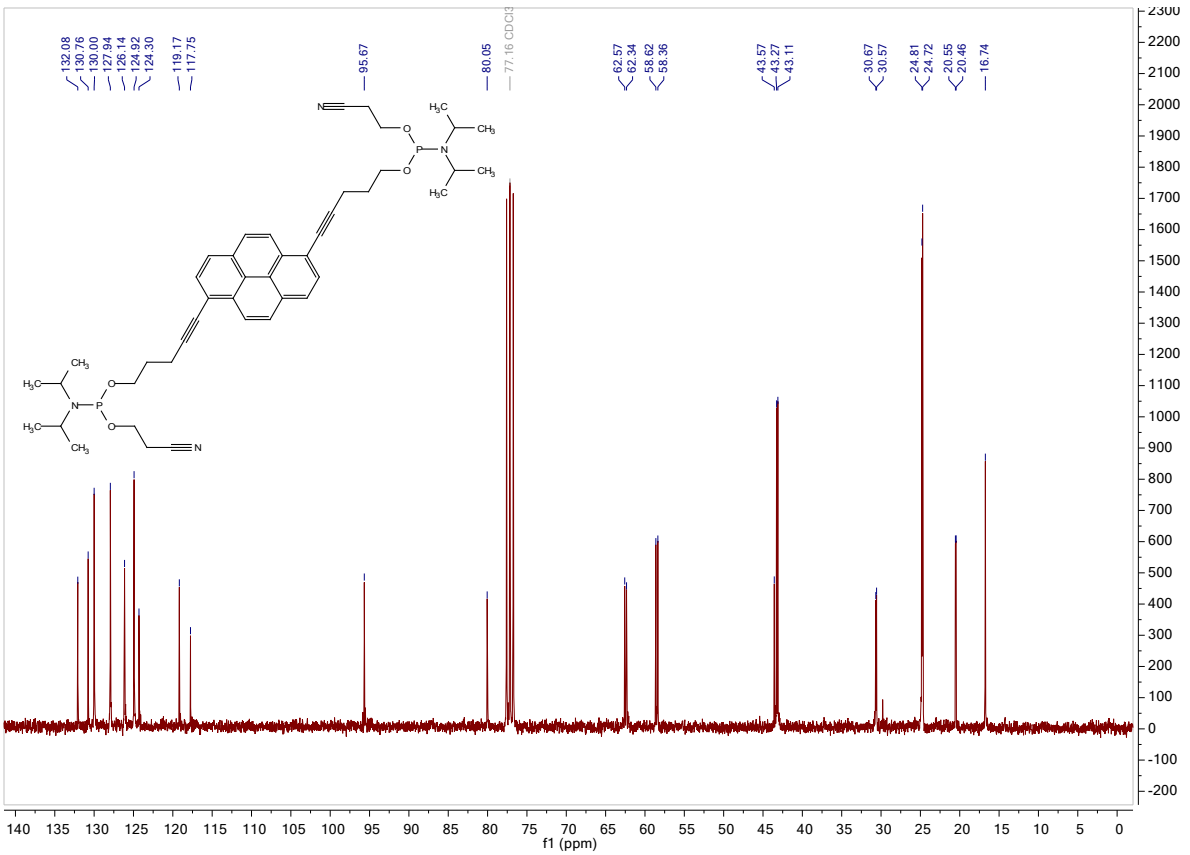


Figure S14. ^{13}C NMR of compound **10** in $CDCl_3$.

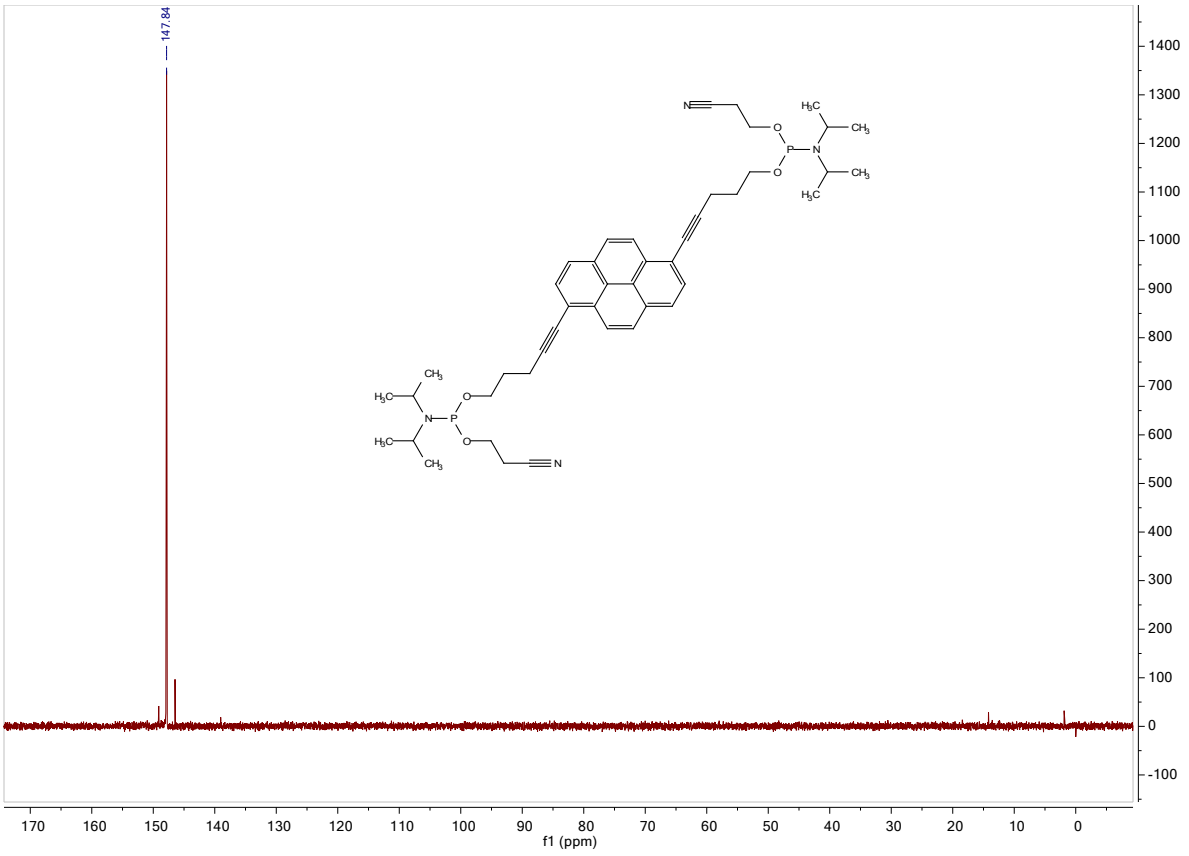


Figure S15. ^{31}P NMR of compound **10** in $CDCl_3$.

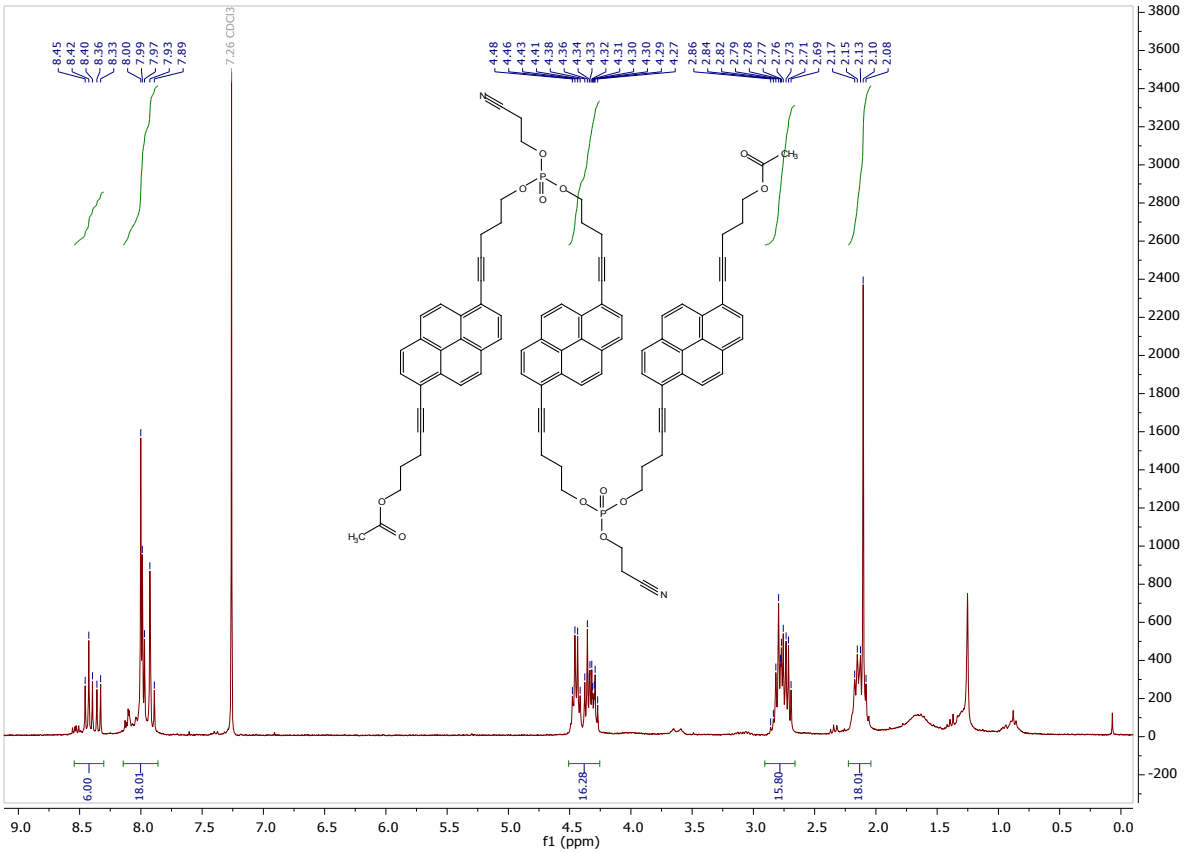


Figure S16. ^{1}H NMR of compound **11** in $CDCl_3$.

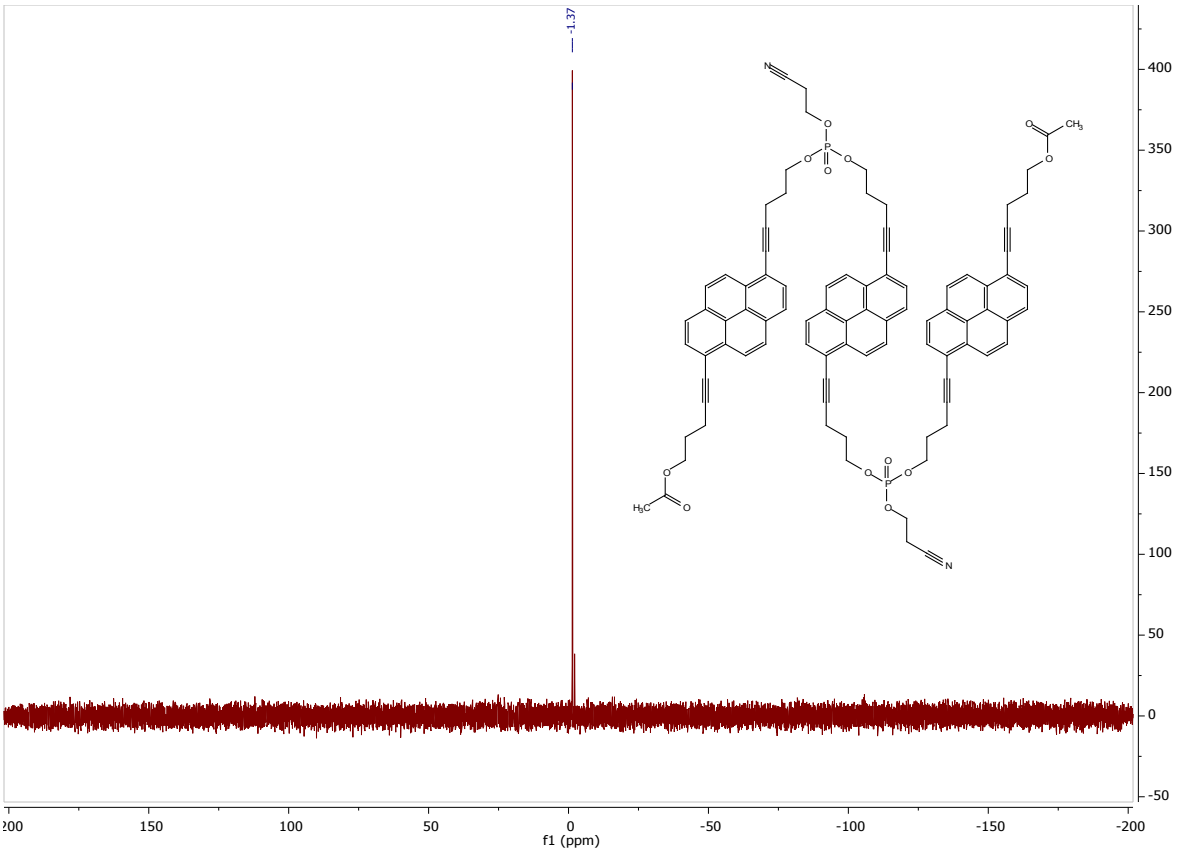


Figure S17. ^{31}P NMR of compound **11** in $CDCl_3$.

5 MS spectra

5.1 N-Phe$_3$

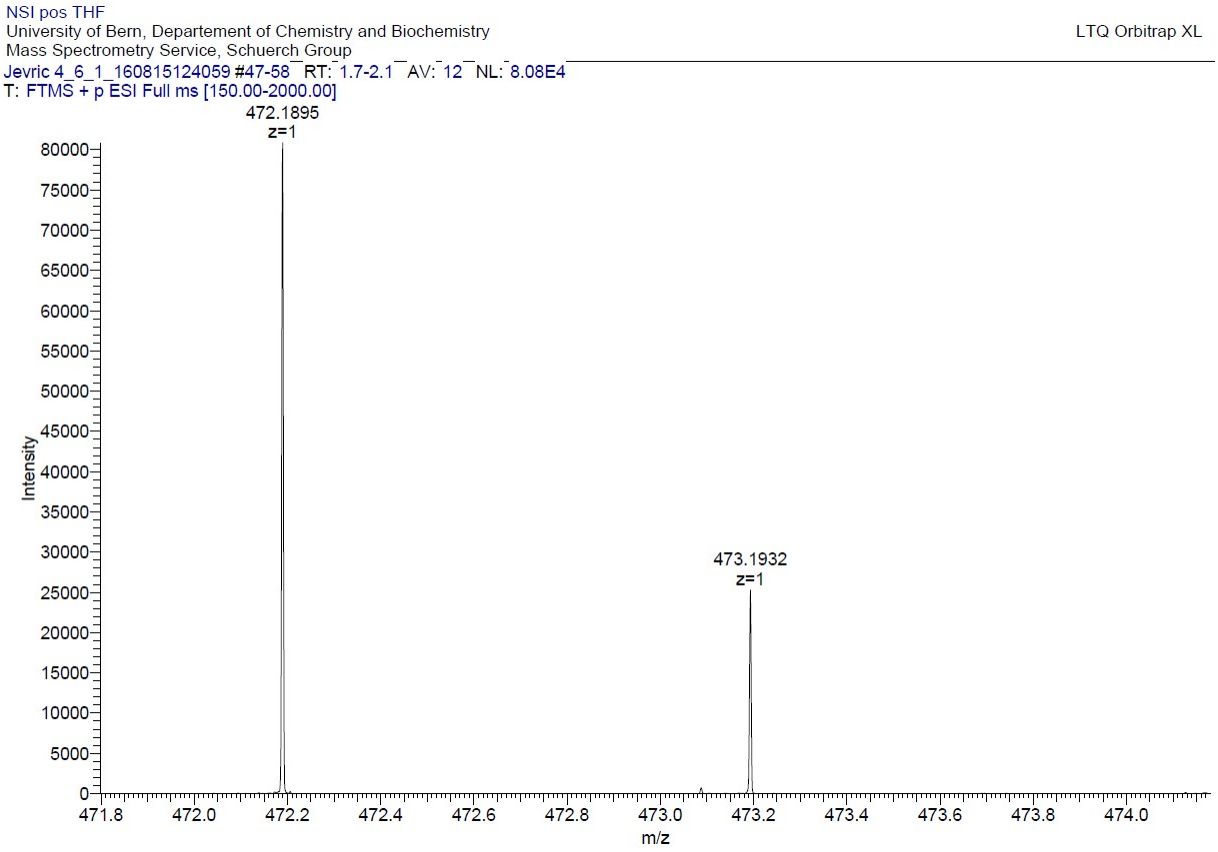


Figure S18. Mass spectrum of compound **3**.

Elemental composition search on mass 472.1895

m/z= 467.1895-477.1895

m/z	Theo. Mass	Delta (ppm)	Composition
472.1895	472.1894	0.28	$C_{30}H_{24}O_2N_4$
	472.1883	2.53	$C_{30}H_{27}O_3NNa$
	472.1907	-2.56	$C_{32}H_{26}O_3N$
	472.1880	3.11	$C_{29}H_{28}O_6$
	472.1910	-3.15	$C_{33}H_{25}N_2Na$
	472.1870	5.37	$C_{28}H_{25}O_2N_4Na$
	472.1867	5.96	$C_{27}H_{26}O_5N_3$
	472.1856	8.21	$C_{27}H_{29}O_6Na$
	472.1934	-8.24	$C_{35}H_{24}N_2$
	472.1843	11.05	$C_{25}H_{27}O_5N_3Na$

Figure S19. Elemental composition of compound **3**.

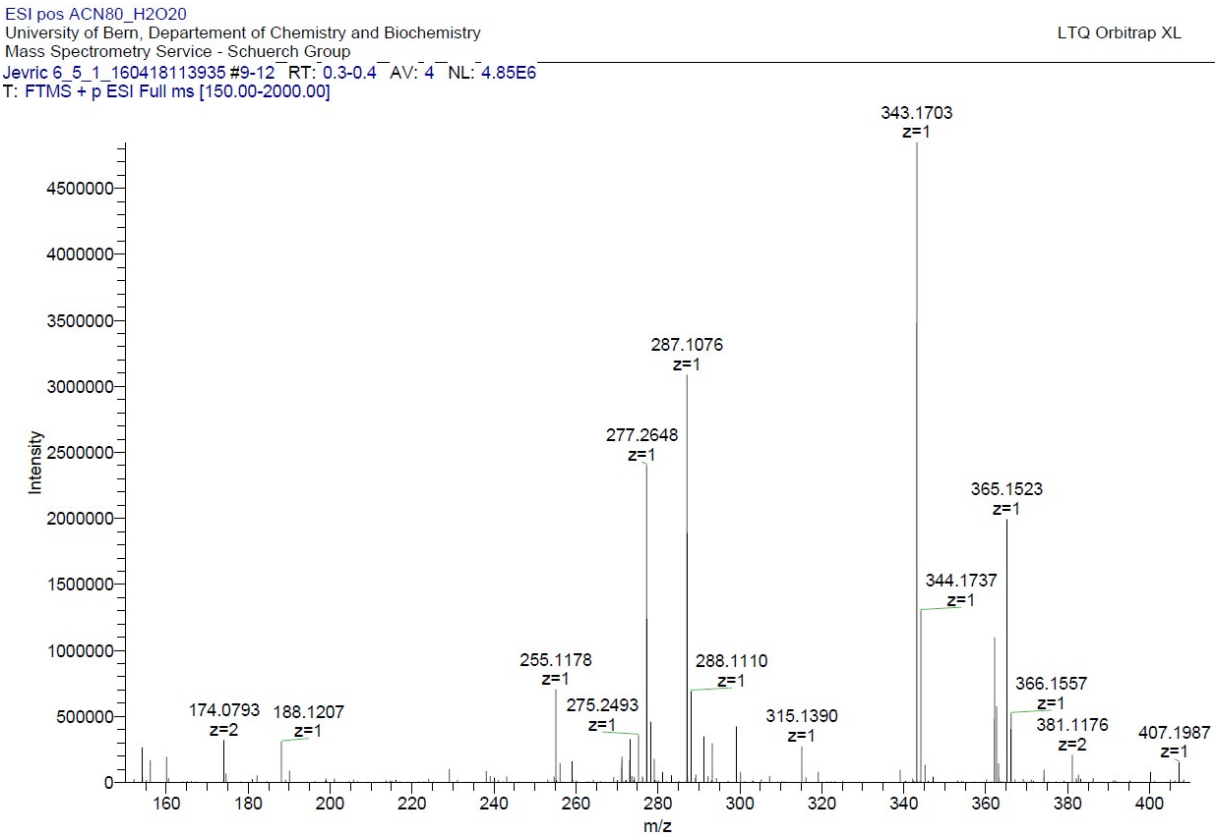


Figure S20. Mass spectrum of compound **4**.

Elemental composition search on mass 343.1703

m/z= 338.1703-348.1703

m/z	Theo. Mass	Delta (ppm)	Composition
343.1703	343.1693	3.13	$C_{24}H_{23}O_2$
	343.1669	10.14	$C_{22}H_{24}O_2Na$
	343.1781	-22.60	$C_{21}H_{24}ON_2Na$
	343.1805	-29.61	$C_{23}H_{23}ON_2$
	343.1567	39.77	$C_{23}H_{21}O_2N$
	343.1543	46.78	$C_{21}H_{22}O_2NNa$

Figure S21. Elemental composition of compound **4**.

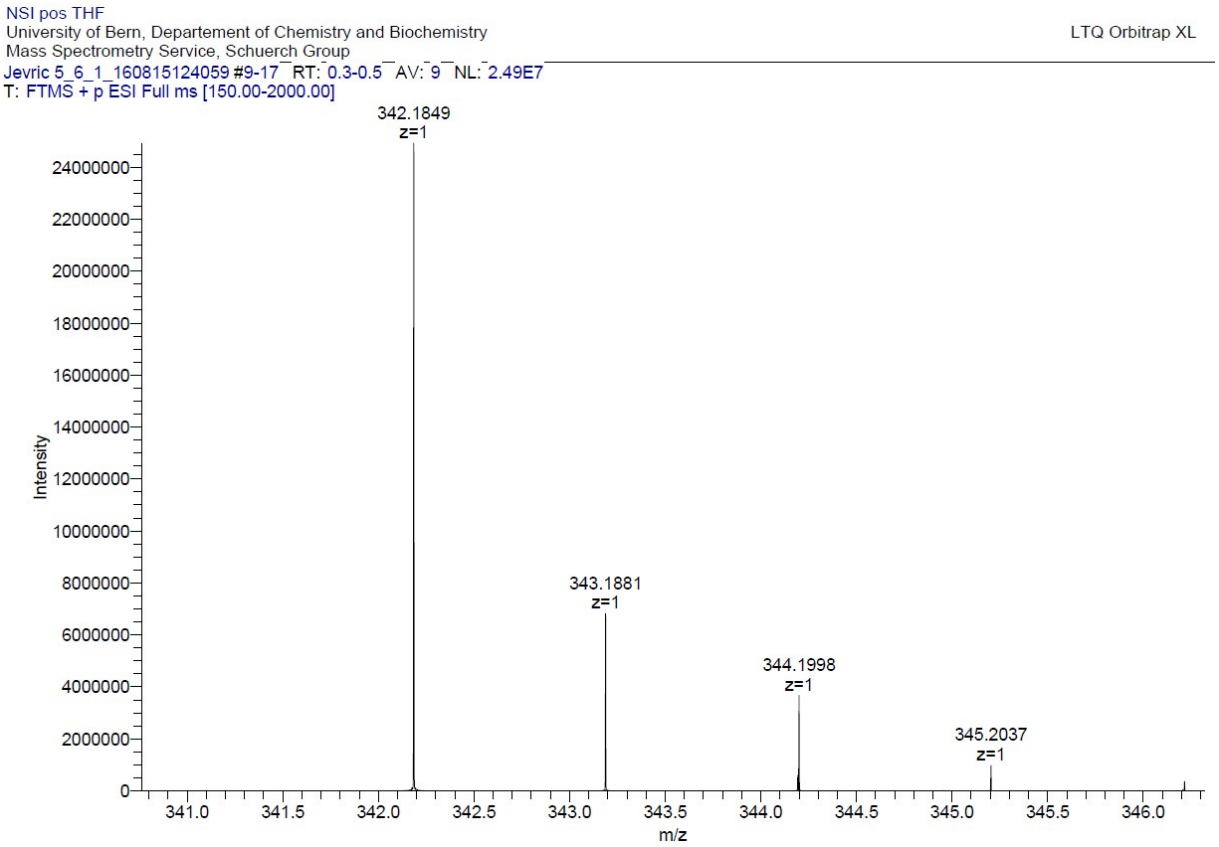


Figure S22. Mass spectrum of compound **5**.

Elemental composition search on mass 342.1849

m/z= 337.1849-347.1849

m/z	Theo. Mass	Delta (ppm)	Composition
342.1849	342.1852	-0.88	$C_{24}H_{24}ON$
	342.1839	3.04	$C_{22}H_{22}N_4$
	342.1828	6.15	$C_{22}H_{25}ONNa$
	342.1826	6.95	$C_{21}H_{26}O_4$
	342.1874	-7.09	$C_{13}H_{27}O_5N_4Na$
	342.1815	10.07	$C_{20}H_{23}N_4Na$
	342.1812	10.88	$C_{19}H_{24}O_3N_3$
	342.1887	-11.01	$C_{15}H_{29}O_6NNa$
	342.1802	13.98	$C_{19}H_{27}O_4Na$
	342.1898	-14.12	$C_{15}H_{26}O_5N_4$

Figure S23. Elemental composition of compound **5**.

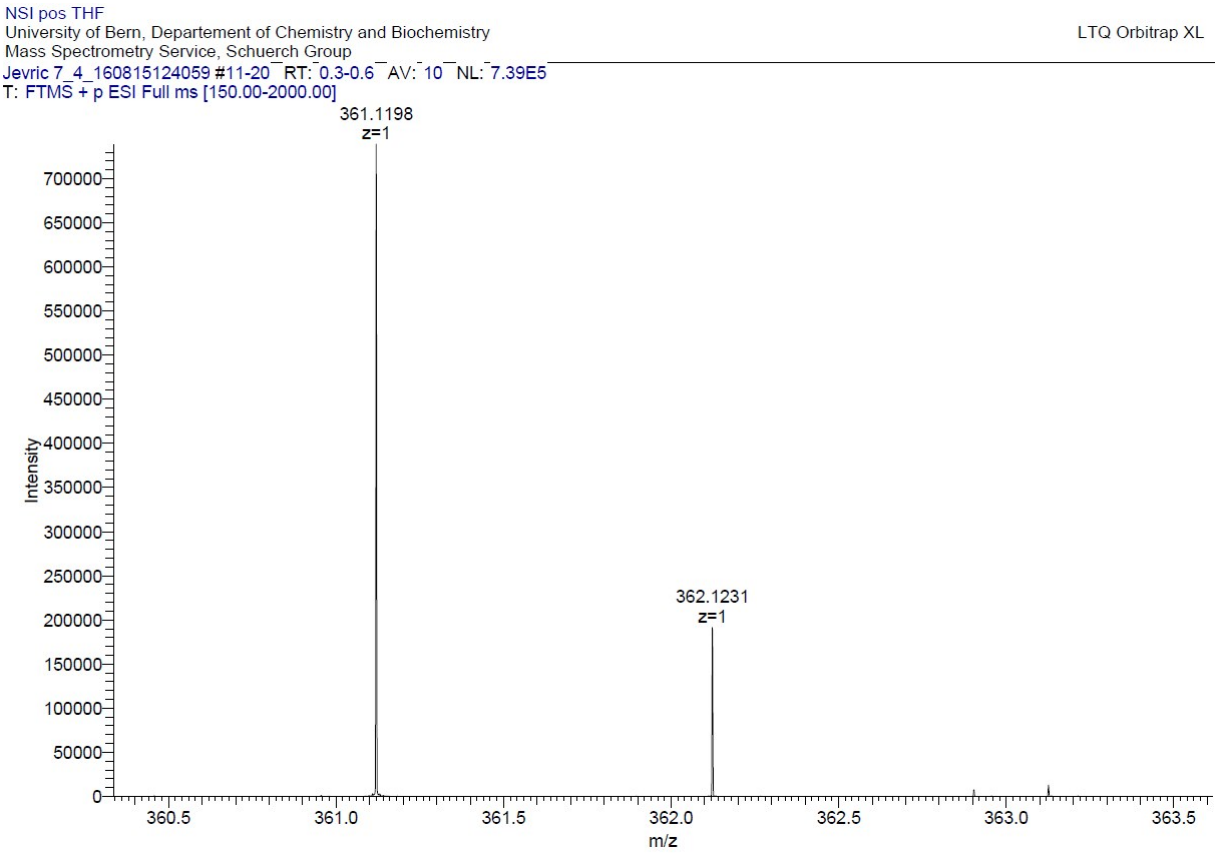


Figure S24. Mass spectrum of compound **6**.

Elemental composition search on mass 361.1198

m/z= 356.1198-366.1198

m/z	Theo. Mass	Delta (ppm)	Composition
361.1198	361.1199	-0.31	$C_{24}H_{18}O_2Na$
	361.1210	-3.25	$C_{24}H_{15}ON_3$
	361.1186	3.41	$C_{22}H_{16}ON_3Na$
	361.1183	4.17	$C_{21}H_{17}O_4N_2$
	361.1223	-6.97	$C_{26}H_{17}O_2$
	361.1159	10.83	$C_{19}H_{18}O_4N_2Na$
	361.1244	-12.85	$C_{15}H_{20}O_6N_3Na$
	361.1143	15.31	$C_{16}H_{17}O_6N_4$
	361.1268	-19.51	$C_{17}H_{19}O_6N_3$

Figure S25. Elemental composition of compound **6**.

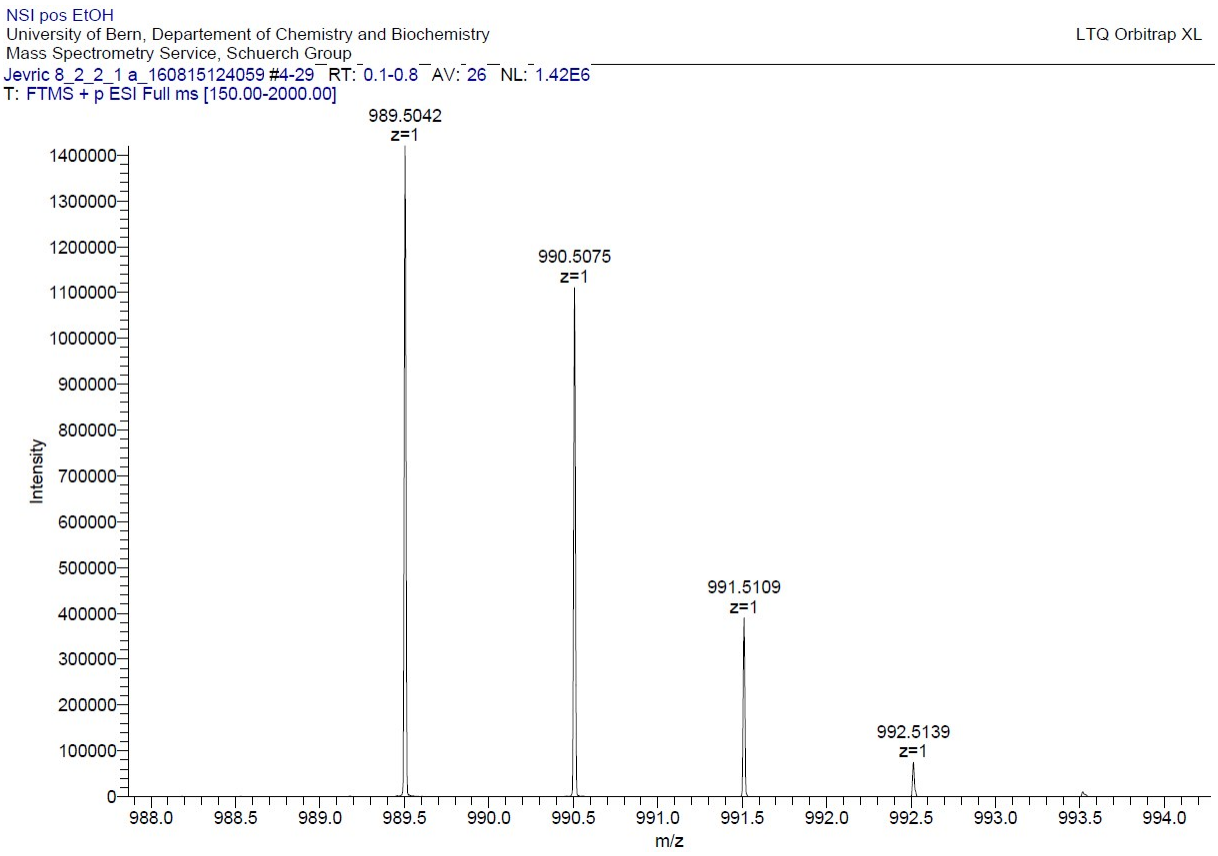


Figure S26. Mass spectrum of compound **N-Phe$_3$**.

Elemental composition search on mass 989.5042

m/z= 984.5042-994.5042

m/z	Theo. Mass	Delta (ppm)	Composition
989.5042	989.5041	0.13	$C_{72}H_{65}O_2N_2$
	989.5057	-1.51	$C_{75}H_{66}Na$
	989.5017	2.56	$C_{70}H_{66}O_2N_2Na$
	989.5014	2.83	$C_{69}H_{67}O_5N$
	989.5000	4.19	$C_{67}H_{65}O_4N_4$
	989.4990	5.26	$C_{67}H_{68}O_5NNa$
	989.5102	-6.09	$C_{66}H_{68}O_4N_3Na$
	989.4976	6.62	$C_{65}H_{66}O_4N_4Na$
	989.5115	-7.44	$C_{68}H_{70}O_5Na$
	989.5126	-8.52	$C_{68}H_{67}O_4N_3$

Figure S27. Elemental composition of compound **N-Phe$_3$**.

5.2 Py_3

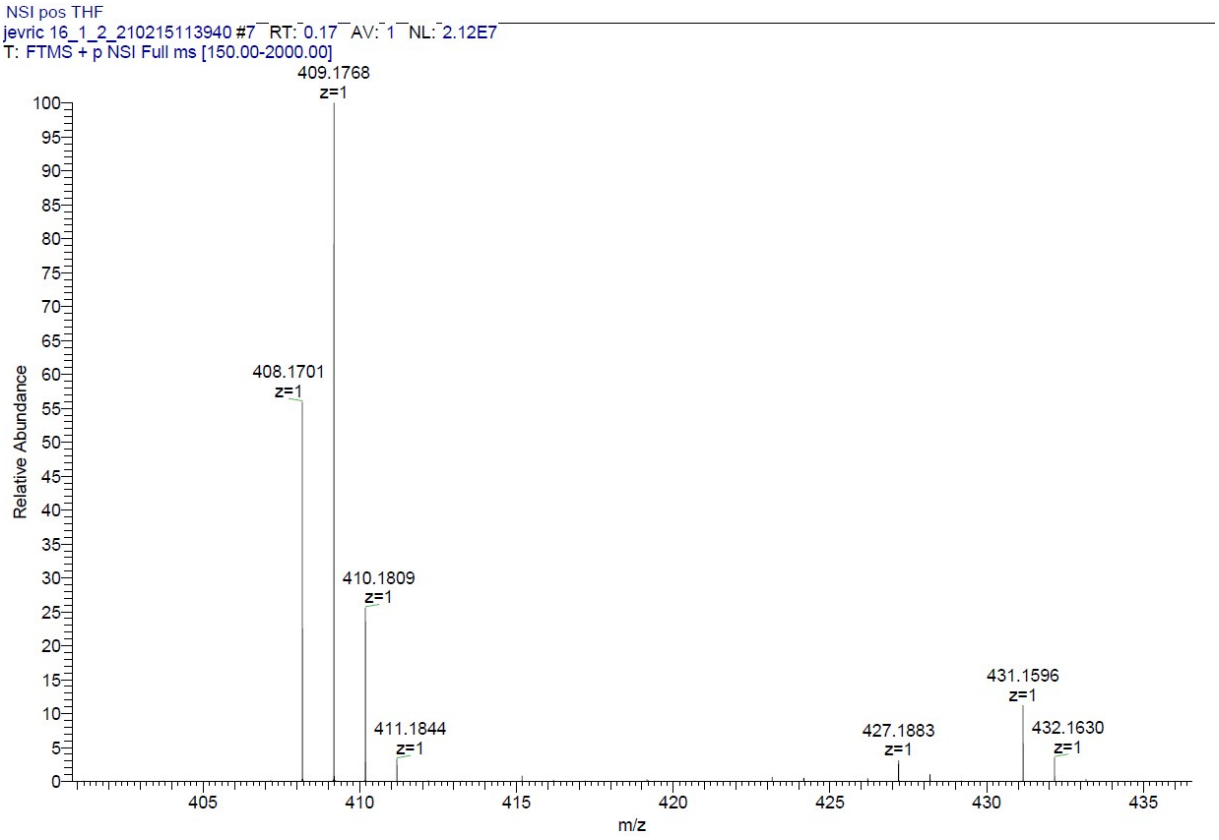


Figure S28. Mass spectrum of compound **9**.

Elemental composition search on mass 408.1701

m/z= 403.1701-413.1701

m/z	Theo. Mass	Delta (ppm)	Composition
408.1701	408.1696	1.35	$C_{26}H_{25}O_3Na$
	408.1720	-4.55	$C_{28}H_{24}O_3$
	408.1675	6.40	$C_{27}{}^{13}CH_{23}O_3$
	408.1651	12.30	$C_{25}{}^{13}CH_{24}O_3Na$

Figure S29. Elemental composition of compound **9**.

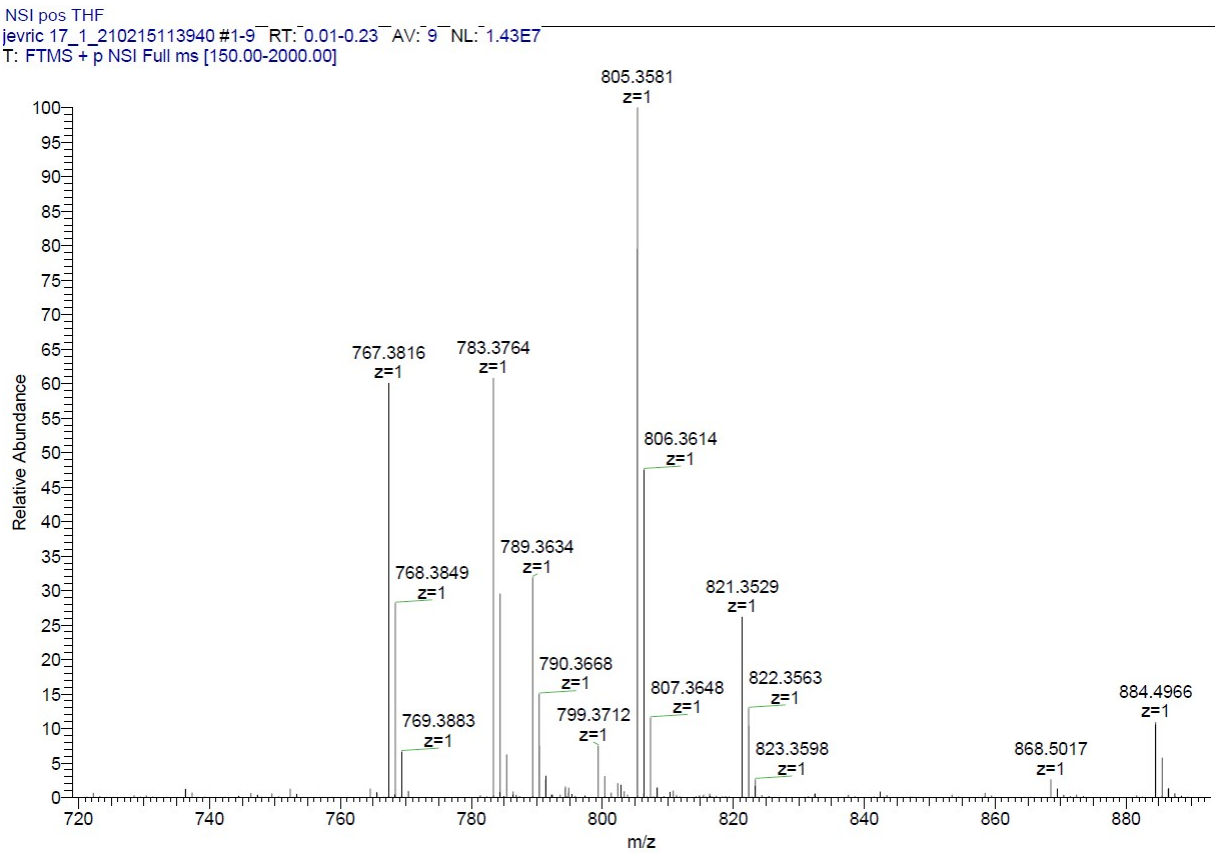


Figure S30. Mass spectrum of compound **10**.

Elemental composition search on mass 767.3816

m/z= 762.3816-772.3816

m/z	Theo. Mass	Delta (ppm)	Composition
767.3816	767.3826	-1.26	$C_{42}H_{58}O_4N_4NaP_2$
	767.3850	-4.40	$C_{44}H_{57}O_4N_4P_2$
	767.3951	-17.65	$C_{43}H_{60}O_4N_3NaP_2$

Figure S31. Elemental composition of compound **10**.

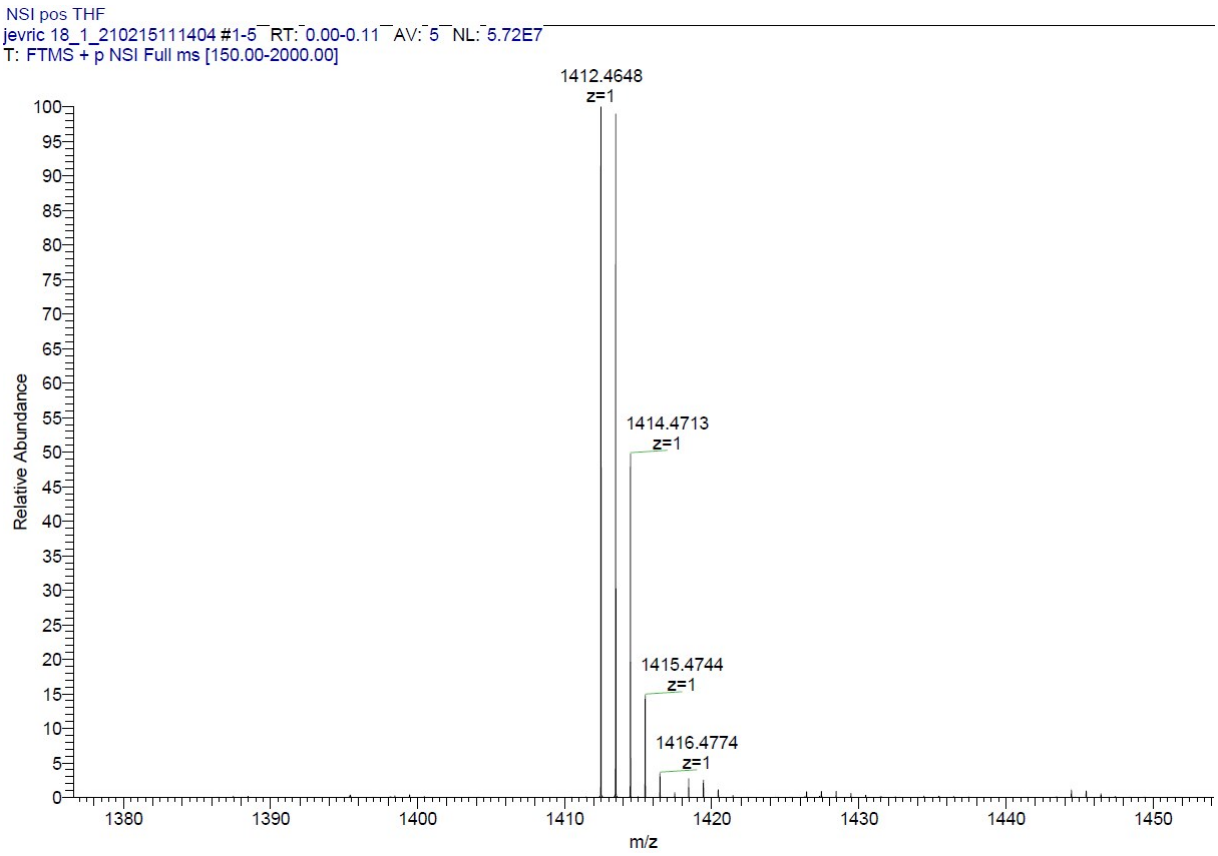


Figure S32. Mass spectrum of compound **11**.

Elemental composition search on mass 1412.4648

m/z= 1407.4648-1417.4648

m/z	Theo. Mass	Delta (ppm)	Composition
1412.4648	1412.4687	-2.80	$C_{86}H_{75}O_{12}N_2NaP_2$
	1412.4712	-4.50	$C_{88}H_{74}O_{12}N_2P_2$
	1412.4813	-11.70	$C_{87}H_{77}O_{12}NNaP_2$

Figure S33. Elemental composition of compound **11**.

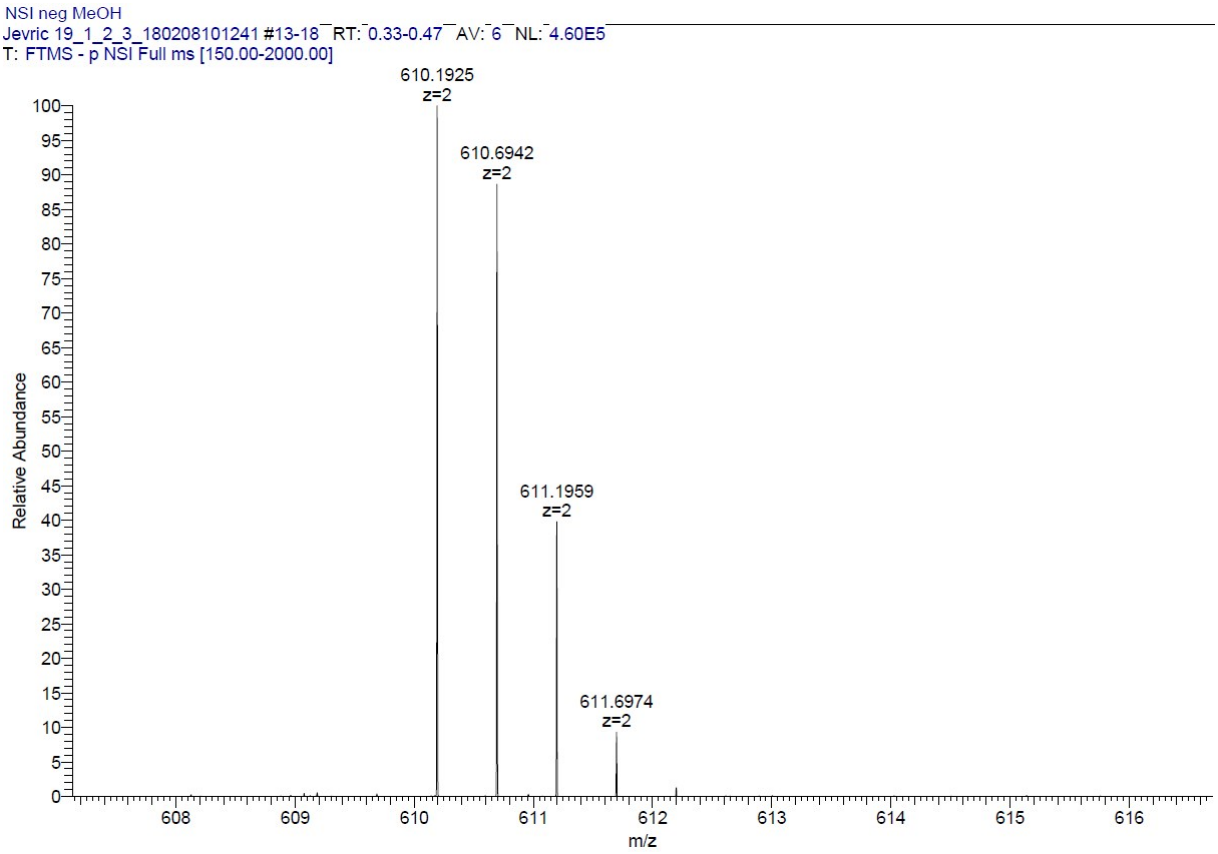


Figure S34. Mass spectrum of compound **Py_3**.

6 UV-vis and fluorescence spectra

6.1 N-Phe_3

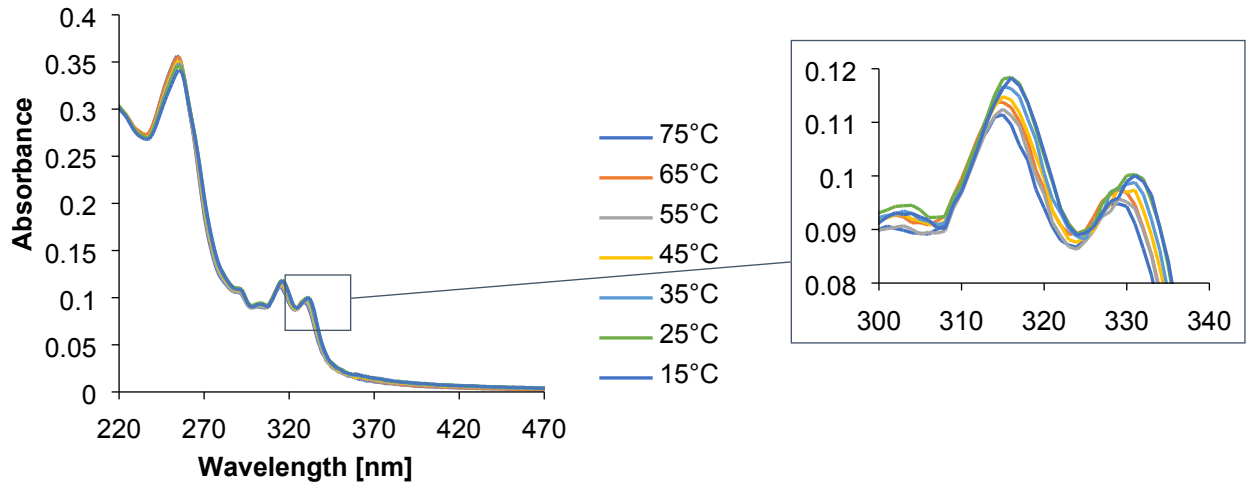


Figure S35. Absorption spectra of **N-Phe_3** in aqueous medium when cooling down from 75 °C to 15 °C in 10 °C steps. A red-shift of 2 nm is observed between 45 °C and 35 °C. Conditions: 1 µM **N-Phe_3**, 10 mM sodium acetate buffer, 10 vol% ethanol.

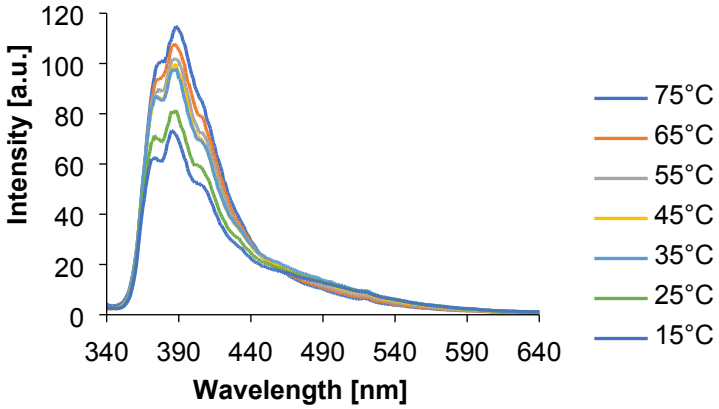


Figure S36. Fluorescence spectra of **N-Phe$_3$** in aqueous medium measured every 10 °C. Conditions: 1 μM **N-Phe$_3$**, 10 mM sodium acetate buffer, 10 vol% ethanol, λ_{ex} = 330 nm.

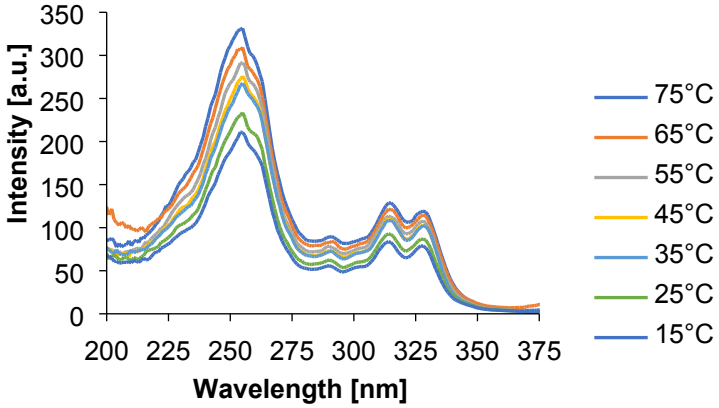


Figure S37. Excitation spectra of **N-Phe$_3$** in aqueous medium measured every 10 °C. Conditions: 1 μM **N-Phe$_3$**, 10 mM sodium acetate buffer, 10 vol% ethanol, λ_{em} = 387 nm.

7 TEM measurements of N-Phe$_3$

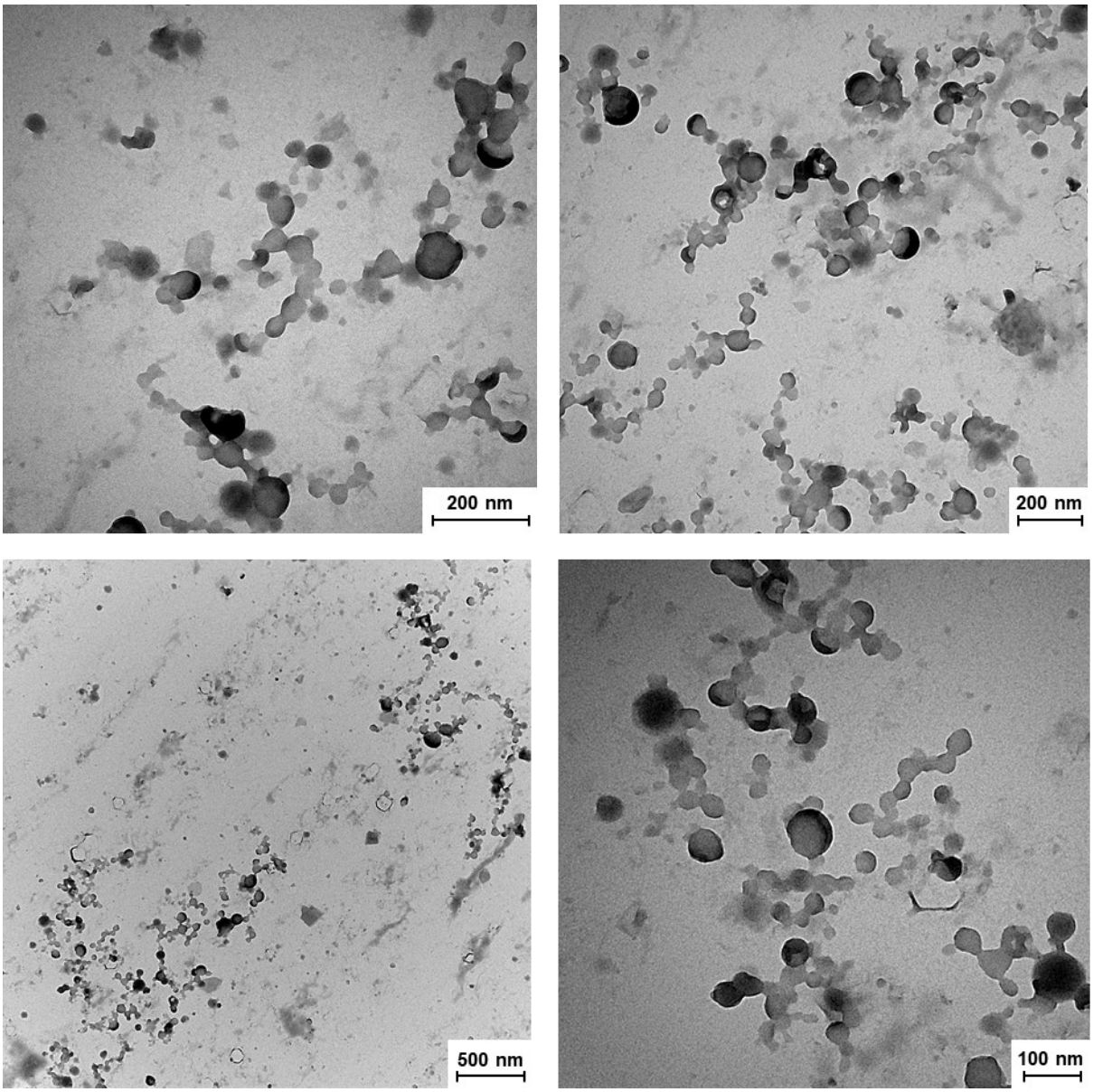


Figure S38. TEM measurements of the self-assembled **N-Phe$_3$** in aqueous medium. Conditions: 5 µM **N-Phe$_3$**, 10 mM sodium acetate buffer (pH 4.7), 10 vol% ethanol.

8 DLS measurements of N-Phe$_3$

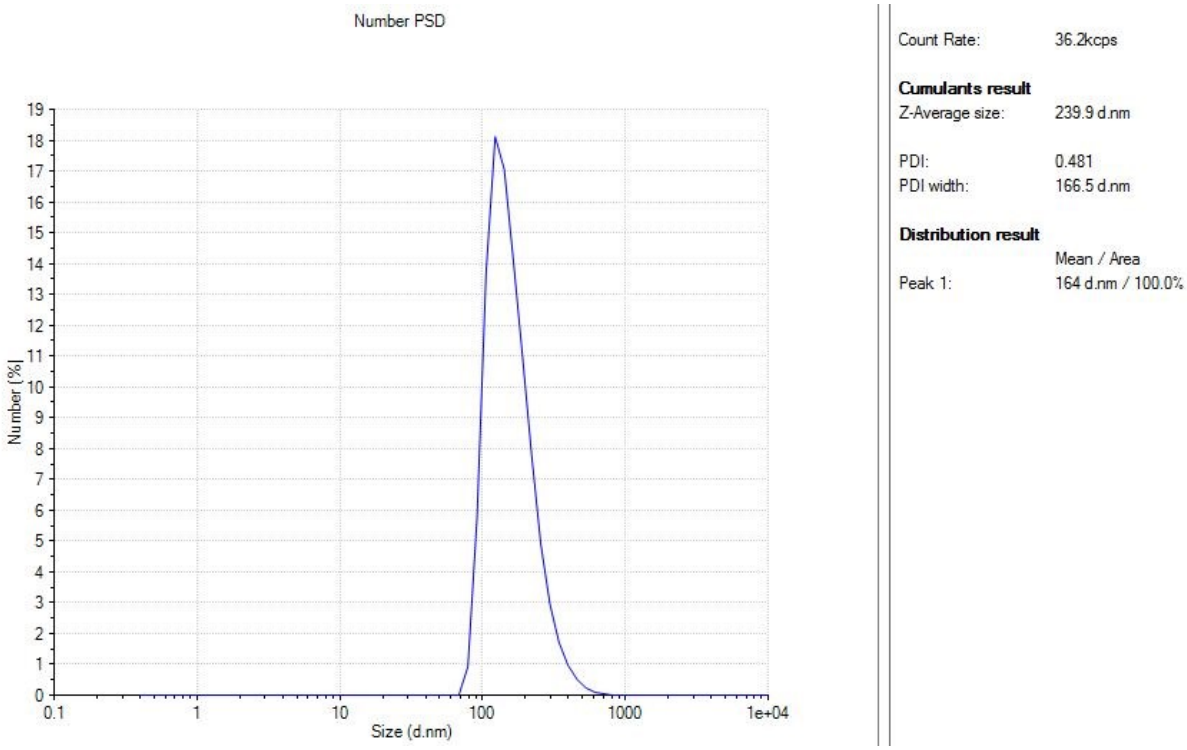


Figure S39. Dynamic light scattering (DLS) measurement of the assembled **N-Phe$_3$** in aqueous medium at 20 °C. Conditions: 10 mM sodium acetate buffer (pH 4.71), 10 vol% ethanol, 1 µM **N-Phe$_3$**.

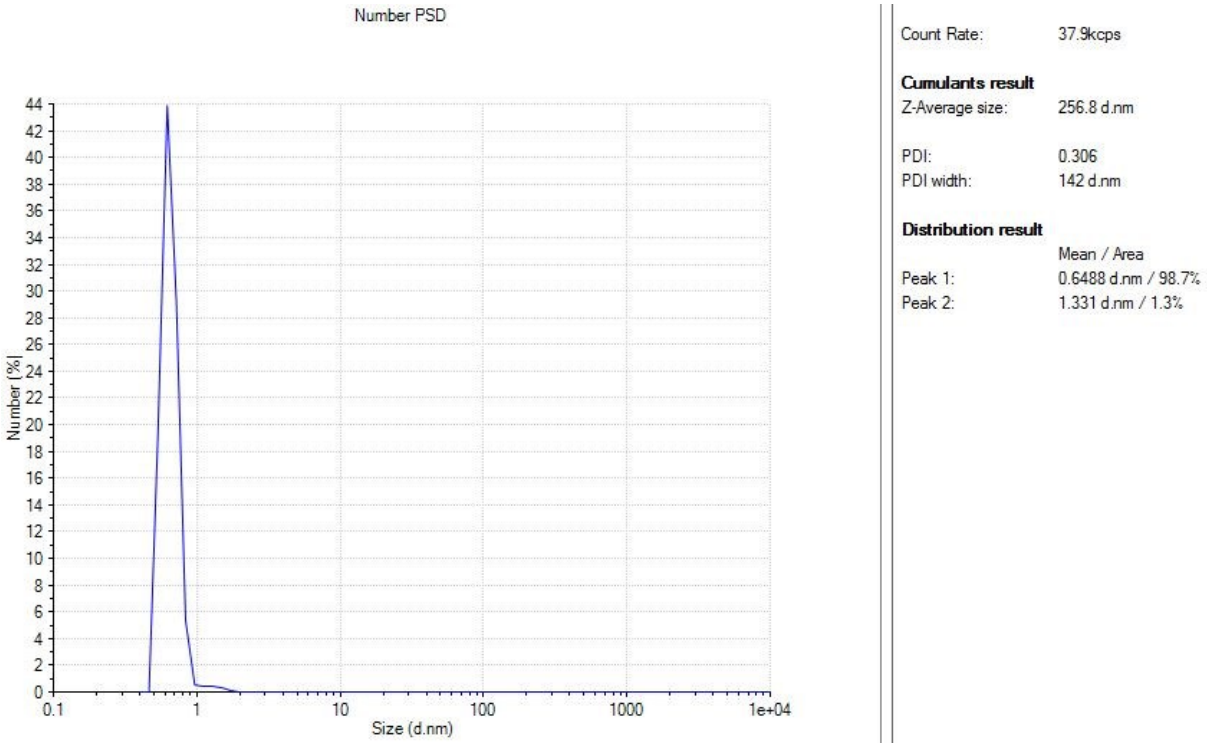


Figure S40. DLS measurement of the disassembled **N-Phe$_3$** in aqueous medium at 70 °C. Conditions: 10 mM sodium acetate buffer (pH 4.71), 10 vol% ethanol, 1 µM **N-Phe$_3$**.

9 Size distribution measurement

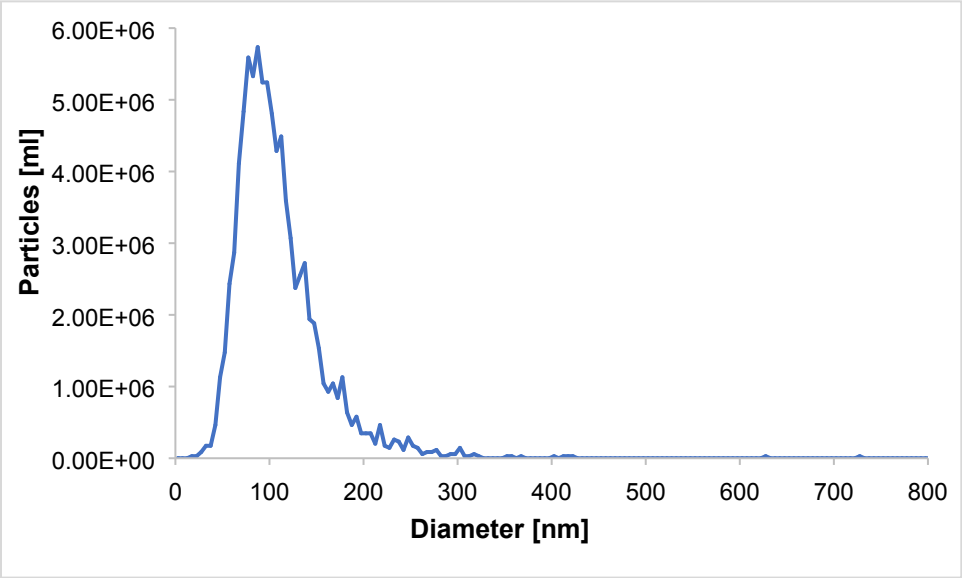


Figure S41. Size distribution profile of the assembled **N-Phe$_3$** (1 µM) in 10 mM sodium acetate buffer (pH 4.7) and 10 % ethanol at 20°C. The mean value is 109.6 nm. The measurement was done with the nanoparticle tracking analysis instrument from ZetaView.

10 Electrostatic assembly experiments

10.1 1. Py$_3$ + 2. N-Phe$_3$

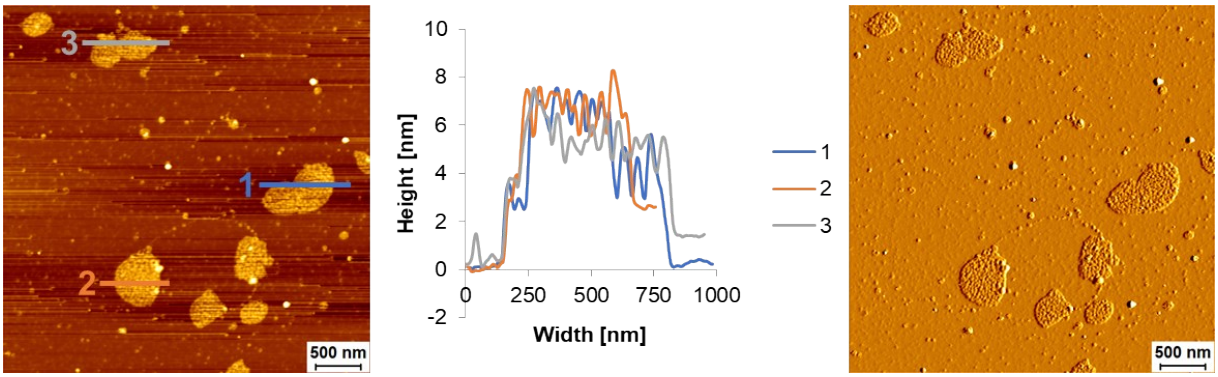


Figure S42. AFM measurements of the two layers: 1. **Py$_3$** + 2. **N-Phe$_3$**, their height profiles and the deflection scan (right). Conditions: 1st layer 2µM **Py$_3$**, 10 mM sodium phosphate buffer (pH 7.1), 10 mM sodium chloride and 10 vol% ethanol, 2nd layer 10 µM **N-Phe$_3$**, 10 mM sodium acetate buffer (pH 4.7) and 10 vol% ethanol.

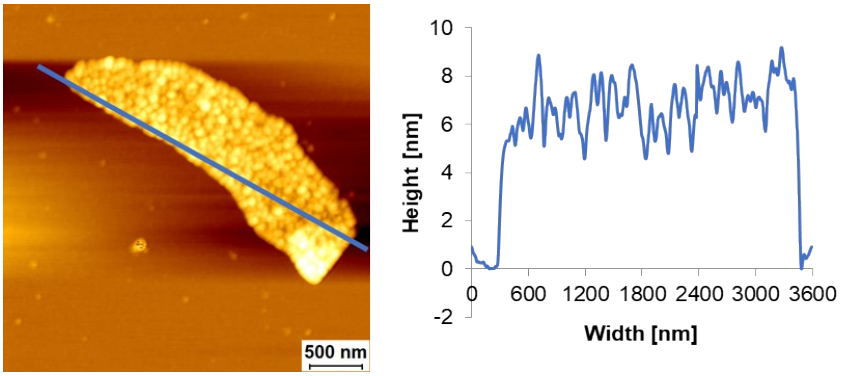


Figure S43. AFM measurement of the two layers: 1. **Py$_3$** + 2. **N-Phe$_3$** and their height profile. Conditions: 1st layer 2µM **Py$_3$**, 10 mM sodium phosphate buffer (pH 7.1), 10 mM sodium chloride and 10 vol% ethanol, 2nd layer 10 µM **N-Phe$_3$**, 10 mM sodium acetate buffer (pH 4.7) and 10 vol% ethanol.

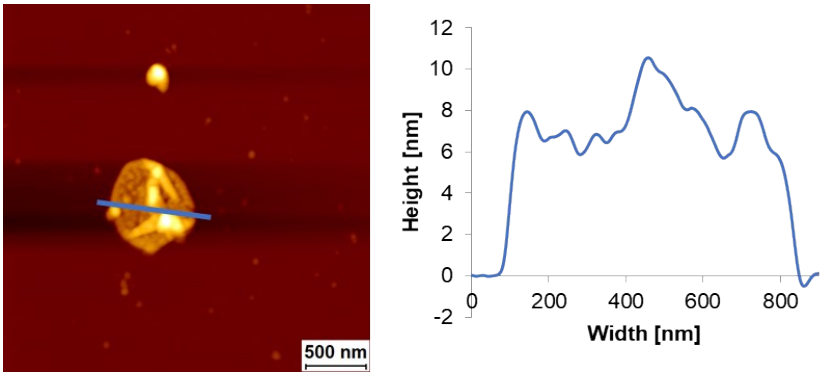


Figure S44. AFM measurement of the two layers: 1. **Py_3** + 2. **N-Phe_3** and their height profile. Conditions: 1st layer 2µM **Py_3**, 10 mM sodium phosphate buffer (pH 7.1), 10 mM sodium chloride and 10 vol% ethanol, 2nd layer 10 µM **N-Phe_3**, 10 mM sodium acetate buffer (pH 4.7) and 10 vol% ethanol.

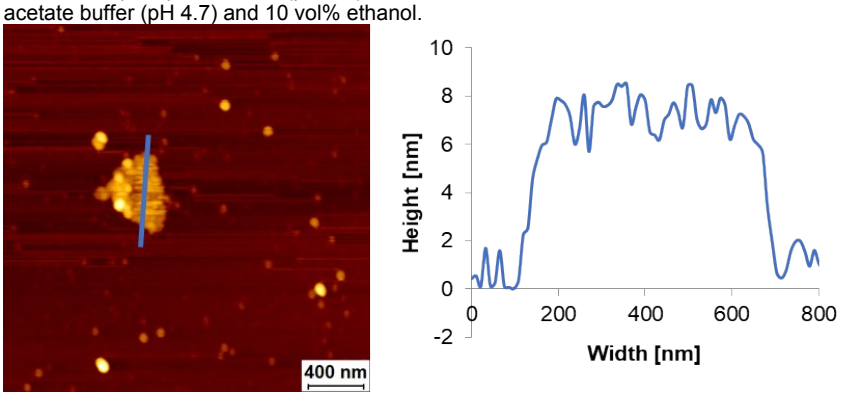


Figure S45. AFM measurement of the two layers: 1. **Py_3** + 2. **N-Phe_3** and their height profile. Conditions: 1st layer 2µM **Py_3**, 10 mM sodium phosphate buffer (pH 7.1), 10 mM sodium chloride and 10 vol% ethanol, 2nd layer 10 µM **N-Phe_3**, 10 mM sodium acetate buffer (pH 4.7) and 10 vol% ethanol.

11 Bibliography

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[3] S. D. Meyer, S. L. Schreiber, *J. Org. Chem.* **1994**, *59*, 7549–7552.

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