

Electronic Supplementary Information

Biomimetic Self-assembling Acylphthalocyanines

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1. Methods, Materials and Analytical Data

All chemicals were purchased from Sigma Aldrich and were used without further purification. Reactions were magnetically stirred under argon atmosphere unless otherwise stated, and monitored by thin-layer chromatography (TLC) MERCK silica gel 60 F₂₅₄ TLC aluminum sheets, the components were visualized by observation under UV light at $\lambda = 254$ nm. Volatile solvents were removed *via* reduced distillation by a Büchi rotary evaporator at appropriate temperature and pressure. Flash column chromatography was performed on Merck silica gel 60 (0.040-0.063 μm). The yields were calculated based on chromatographically purified isolated compounds or isomeric mixtures. *n*-Heptane and CH_2Cl_2 used for self-assembly experiments were dried on 3 Å molecular sieves according to the study of Williams and Lawton,^[1] this provides even drier solvents than the conventional distillation from sodium benzophenone-ketyl or calcium hydride, respectively.

¹H-NMR and ¹³C-NMR spectra were measured out at room temperature on a Bruker Avance Ultrashield NMR spectrometers at 300 or 400 MHz. Chemical shifts are given in ppm relative to residual peaks of CDCl_3 ($\delta = 7.26$ as the internal standard for ¹H of CHCl_3 and $\delta = 77.16$ for ¹³C of CHCl_3). The constants of coupling are given in Hertz (Hz). The abbreviations used to explain the multiplicities are: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal. Mass spectrometric analyses were acquired as high resolution using electrospray (ESI) or matrix-assisted laser desorption ionization (MALDI) on a QStar Elite (Applied Biosystem SCIEX) spectrometer or on a SYNAPT G2 HDMS (Waters) spectrometer at the Spectropole, Campus Scientifique de Saint Jérôme in Marseille. UV-Visible spectra and fluorescence emission of **ZnPc-5a-d** were recorded with a Shimadzu UV-2401 (PC) instrument and JASCO spectrofluorimeter ETC-815, respectively. UV-Vis measurements of the self-assemblies in *n*-heptane at variable temperature were performed on a JASCO V-670 UV-Vis-NIR spectrometer equipped with a Peltier sample holder

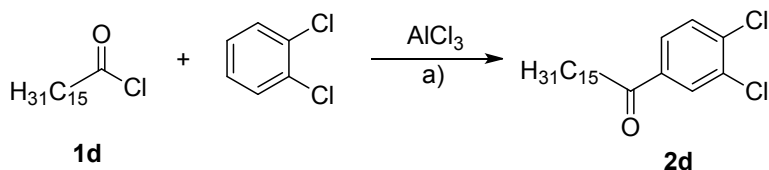
For the temperature-variable UV-Vis measurements, aggregates often formed in the quartz cuvette and when these macro-structures pass the light beam, very noisy, erratic absorbances are measured by the detector. So, magnetic stirring (CCW at 500 rpm) with a rectangular 10×10 mm cm Hellma quartz Suprasil Cuvette covered by a Teflon lid and a Teflon septum was adopted. The fluorescence emission spectra of the disassembly process of **ZnPc-6d** were performed on a JASCO-spectrofluorimeter ETC-815.

[1] D. B. G. Williams, M. Lawton, *J. Org. Chem.* **2010**, 75, 8351-8354.

2. Experimental Data

Experimental Procedures

Synthesis of 1,2-dichloro-4-palmitoylbenzene (2d):



In a dry 250 mL three-neck flask equipped with thermometer, reflux condenser (under argon) and dropping funnel, AlCl_3 (17.73 g, 0.13 mol) was suspended in 50 mL of 1,2-dichlorobenzene and cooled on ice-water bath to 0°C . Then palmitoyl chloride **1d** (35.63 g, 0.13 mol) was added slowly, dropwise under vigorous stirring. After removal of the ice-bath, the resulting mixture was left to warm to room temperature and then gently heated to $100\sim 105^\circ\text{C}$. During this time the color changed from ocher to dark red. After 5 hours heating the reaction mixture was allowed to reach room temperature and left under stirring overnight. To decompose the complex, this mixture was cautiously added into 200 g of ice (containing two drops of 35% hydrochloric acid) under stirring. The mixture became a mustard-colored paste which was extracted in ethyl acetate. The organic layer was then removed in a separating funnel and washed to neutrality with saturated sodium hydrogencarbonate solution and water. After drying over sodium sulphate, the ethyl acetate was evaporated off. The remaining 1,2-dichlorobenzene was distilled off under reduced pressure. The residue was chromatographed through a column (length = 20 cm, diameter = 5 cm) on silica gel with dichloromethane and *n*-hexane (v:v = 1:2) as eluent. $R_f = 0.39$. Yield: 17.13 g, 34%.

^1H NMR (CDCl_3 , 400 MHz,) δ (ppm): 8.00 (1H, d, $J = 1.3$ Hz, ArH), 7.75 (1H, dd, $J = 8.3$ Hz, 1.5 Hz, ArH), 7.50 (1H, d, $J = 8.3$ Hz, ArH), 2.89 (2H, t, $J = 7.3$ Hz, $-\text{CH}_2-$), 1.70 (2H, dt, $J = 14.4, 7.1$ Hz, $-\text{CH}_2-$), 1.45-1.08 (24H, m, $-\text{CH}_2-$), 0.87 (3H, dd, $J = 13.9, 7.7$ Hz, $-\text{CH}_3$).

^{13}C NMR (CDCl_3 , 101 MHz) δ (ppm): 198.09, 137.45, 136.70, 133.32, 130.74, 130.14, 127.16, 38.69, 32.21, 29.81, 29.80, 29.78, 29.73, 29.60, 29.56, 29.48, 29.36, 24.21, 22.87, 14.22.

For the preparation of the compounds **2a**, **2b**, **2c**, the procedure was the same as for compound **2d**.

Synthesis of 1, 2-dichloro-4-acetylbenzene (2a):

The compound **2a** was obtained using acetyl chloride (10.21 g, 0.13 mol). $R_f(\text{CH}_2\text{Cl}_2) = 0.38$. Yield: 22.85 g, 93%.

$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ (ppm): 8.02 (1H, d, $J = 1.9$ Hz, ArH), 7.77 (1H, dd, $J = 8.3, 2.0$ Hz, ArH), 7.54 (1H, d, $J = 8.3$ Hz, ArH), 2.58 (3H, s, CH_3).

$^{13}\text{C NMR}$ (CDCl_3 , 101 MHz) δ (ppm): 195.70, 137.71, 136.66, 133.29, 130.77, 130.34, 127.40, 26.59.

Synthesis of 1, 2-dichloro-4-hexanoylbenzene (2b):

Compound **2b**, was afforded by using hexanoyl chloride as acylation agent (17.49 g, 0.13 mol). $R_f(\text{CH}_2\text{Cl}_2:n\text{-hexane}, v:v = 1:2) = 0.59$. Yield: 19.85 g, 62%.

$^1\text{H NMR}$ (CDCl_3 , 400 MHz,) δ (ppm): 7.99 (1H, d, $J = 2.0$ Hz, ArH), 7.75 (1H, dd, $J = 8.4, 2.0$ Hz, ArH), 7.51 (1H, d, $J = 8.4$ Hz, ArH), 3.01-2.72 (2H, m, $-\text{CH}_2-$), 1.87-1.54 (2H, m, $-\text{CH}_2-$), 1.47-1.21 (4H, m, $-\text{CH}_2-$), 1.07-0.72 (3H, m, $-\text{CH}_3$).

$^{13}\text{C NMR}$ (CDCl_3 , 101 MHz) δ (ppm): 198.19, 137.46, 136.70, 133.31, 130.76, 130.15, 127.18, 38.66, 31.50, 23.89, 22.59, 14.02.

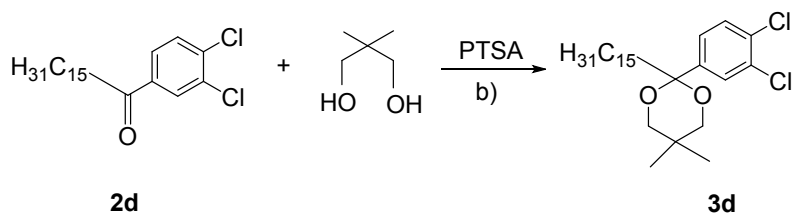
Synthesis of 1,2-dichloro-4-lauroylbenzene (2c):

Lauroyl chloride (28.40 g, 0.13 mol) was used to prepare compound **2c**. $R_f(\text{CH}_2\text{Cl}_2:n\text{-hexane}, v:v = 1:2) = 0.61$. Yield: 25.36 g, 59%.

$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ (ppm): 8.03 (1H, t, $J = 4.2$ Hz, ArH), 7.77 (1H, dd, $J = 8.4, 2.0$ Hz, ArH), 7.54 (1H, d, $J = 8.4$ Hz, ArH), 2.91 (2H, t, $J = 7.4$ Hz, $-\text{CH}_2-$), 1.72 (2H, dt, $J = 14.7, 7.4$ Hz, $-\text{CH}_2-$), 1.25 (16H, s, $-\text{CH}_2-$), 0.88 (3H, t, $J = 6.8$ Hz, $-\text{CH}_3$).

$^{13}\text{C NMR}$ (CDCl_3 , 101 MHz) δ (ppm): 198.36, 137.56, 136.77, 133.39, 130.85, 130.25, 127.24, 38.65, 32.13, 29.76, 29.63, 29.57, 29.48, 29.43, 29.40, 24.06, 22.83, 14.26.

Synthesis of 2-(3,4-dichlorophenyl)-5,5-dimethyl-2-pentadecyl-1,3-dioxane (3d):



1,2-Dichloro-4-palmitoylbenzene **2d** (10.00 g, 25.97 mmol), neopentylglycol (27.01 g, 259.70 mmol), *p*-toluenesulfonic acid (PTSA) (1.61 g, 9.35 mmol) and toluene (150 mL) were placed in a 250 mL flask fitted with a Dean-Stark trap, a reflux condenser and the mixture was heated to reflux for 5 hours. The reaction mixture was cooled at room temperature and was washed with a saturated sodium hydrogencarbonate solution and then with water. After solvent evaporation, the compound **3d** was obtained as a red oil by chromatography on silica gel (length = 20 cm, diameter = 5 cm) with dichloromethane and *n*-hexane (v:v = 1:2) as eluent. $R_f = 0.33$. Yield: 7.71 g, 63%.

$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ (ppm): 7.50-7.40 (2H, m, ArH), 7.22 (1H, d, $J = 8.2$ Hz, ArH), 3.43-3.30 (4H, m, $-\text{CH}_2-$), 1.75-1.61 (2H, m, $-\text{CH}_2-$), 1.42-0.71 (32H, m, $-\text{CH}_2-$ and $-\text{CH}_3$), 0.58 (3H, s, $-\text{CH}_3$). $^{13}\text{C NMR}$ (CDCl_3 , 101 MHz,) δ (ppm): 141.03, 132.89, 131.80, 130.64, 129.56, 127.01, 100.97, 77.16, 71.73, 44.58, 32.06, 30.13, 29.82, 29.81, 29.79, 29.76, 29.74, 29.67, 29.62, 29.54, 29.50, 29.42, 23.02, 22.82, 22.74, 21.98, 14.25.

Using the above procedure, the compounds **3a**, **3b**, **3c**, were obtained in relatively good yields.

Synthesis of 2-(3,4-dichlorophenyl)-2,5,5-trimethyl-1,3-dioxane(3a):

For the preparation of the compound **3a**, 1,2-dichloro-4-acetylbenzene **2a** (10.00 g, 52.9 mmol), neopentylglycol (55.03 g, 529 mmol), *p*-toluenesulfonic acid (3.28 g, 19.04 mmol) were used. R_f (CH_2Cl_2) = 0.48. Yield: 6.94 g, 48%.

$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ (ppm): 7.49 (1H, d, $J = 1.9$ Hz, ArH), 7.43 (1H, d, $J = 8.3$ Hz, ArH), 7.25 (1H, dd, $J = 8.3, 1.9$ Hz, ArH), 3.36 (4H, q, $J = 10.8$ Hz, $-\text{CH}_2-$), 1.49 (3H, s, $-\text{CH}_3$), 1.25 (3H, s, $-\text{CH}_3$), 0.59 (3H, s, $-\text{CH}_3$).

$^{13}\text{C NMR}$ (CDCl_3 , 101 MHz) δ (ppm): 141.81, 133.02, 131.87, 130.89, 129.02, 126.39, 99.43, 71.86, 31.81, 30.03, 22.86, 21.95.

Synthesis of 2-(3,4-dichlorophenyl)-5,5-dimethyl-2-pentyl-1,3-dioxane (3b):

1,2-Dichloro-4-hexanoylbenzene **2b** (10.00 g, 40.8 mmol), neopentylglycol (42.43 g, 408 mmol), *p*-toluenesulfonic acid (5.53 g, 14.7 mmol) were used to afford compound **3b**. R_f ($\text{CH}_2\text{Cl}_2:n$ -hexane, v:v = 1:4) = 0.34. Yield: 7.70 g, 57%.

$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ (ppm): 7.46 (1H, d, $J = 2.0$ Hz, ArH), 7.43 (1H, d, $J = 8.3$ Hz, ArH), 7.21 (1H, dd, $J = 8.3, 2.0$ Hz, ArH), 3.43-3.30 (4H, m, $-\text{CH}_2-$), 1.75-1.63 (2H, m, $-\text{CH}_2-$), 1.43-1.29 (2H, m, $-\text{CH}_2-$), 1.28-1.12 (7H, m, $-\text{CH}_2-$ and $-\text{CH}_3$), 0.82 (3H, t, $J = 7.1$ Hz, $-\text{CH}_3$), 0.58 (3H, s, $-\text{CH}_3$).

$^{13}\text{C NMR}$ (CDCl_3 , 101 MHz) δ (ppm): 141.03, 132.87, 131.79, 130.63, 129.55, 127.01, 100.96, 71.73, 44.53, 31.97, 30.13, 23.01, 22.69, 22.64, 21.97, 14.16.

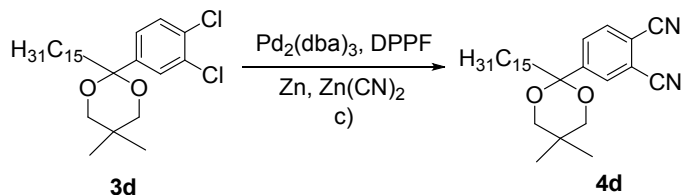
Synthesis of 2-(3,4-dichlorophenyl)-5,5-dimethyl-2-undecyl-1,3-dioxane (3c):

Using 1,2-dichloro-4-lauroylbenzene **2c** (10.00 g, 30.4 mmol), neopentylglycol (31.62 g, 304 mmol), *p*-toluenesulfonic acid (1.89 g, 11.0 mmol) were reacted to give compound **3c**. R_f ($\text{CH}_2\text{Cl}_2:n$ -hexane, v:v = 1:4) = 0.18. Yield: 5.14 g, 41%.

$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ (ppm): 7.45(2H, dd, $J = 10.6, 5.1$ Hz, ArH), 7.22(1H, dd, $J = 8.3, 2.0$ Hz, ArH), 3.49-3.23 (4H, m, $-\text{CH}_2-$), 1.83-1.56 (2H, m, $-\text{CH}_2-$), 1.43-1.08 (21H, m, $-\text{CH}_2-$ and $-\text{CH}_3$), 0.86 (3H, t, $J = 6.8$ Hz, $-\text{CH}_3$), 0.59 (3H, s, $-\text{CH}_3$).

$^{13}\text{C NMR}$ (CDCl_3 , 101 MHz) δ (ppm): 141.01, 132.89, 131.82, 130.68, 129.60, 127.06, 101.02, 71.79, 44.58, 32.06, 30.20, 29.82, 29.76, 29.74, 29.73, 29.68, 29.48, 23.04, 22.83, 22.02, 14.26.

Synthesis of 4-(5,5-dimethyl-2-pentadecyl-1,3-dioxan-2-yl)phthalonitrile (4d):



2-(3,4-Dichlorophenyl)-5,5-dimethyl-2-pentadecyl-1,3-dioxane **3d** (2.0 g, 4.82 mmol), tris(dibenzylideneacetone)-dipalladium(0) ($\text{Pd}_2(\text{dba})_3$) (0.35 g, 0.39 mmol, 8 mol %), 1,1'-bis(diphenyl-phosphino)ferrocene (DPPF) (0.43 g, 0.78 mmol, 16 mol %), active zinc (0.15 g, 2.31 mmol, 48 mol %) and zinc cyanide (0.90 g, 7.71 mmol, 160 mol %) were weighed under nitrogen and added in solid form to a dry 100 mL flask. *N,N*-Dimethylacetamide (DMA, 20 mL) which was initially purged with argon for 5 minutes, was injected via a septum cap. The reaction mixture was stirred at 120 °C under nitrogen for 4 hours. Thereafter, the reaction mixture was left to cool at room temperature overnight under stirring. The reaction mixture was transferred to a separating funnel, diluted with ethyl acetate, and washed with NH_4OH and saturated sodium chloride solution until the pH was neutral. The product was dried over sodium sulphate and the solvent was then vaporized on a rotary evaporator. This was followed by chromatography using a column (length = 30 cm, diameter = 3.5 cm) on silica gel with a mixture of ethyl acetate:*n*-hexane: 1:4 (v:v) as eluent having $R_f = 0.38$. The compound **4d** was recrystallized from toluene to obtain white crystals. Yield: 1.01 g, 39%.

^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 7.83 (2H, d, $J = 6.2$ Hz, ArH), 7.76 (1H, d, $J = 8.1$ Hz, ArH), 3.46 (2H, d, $J = 11.0$ Hz, $-\text{CH}_2-$), 3.22 (2H, d, $J = 11.0$ Hz, $-\text{CH}_2-$), 1.74-1.62 (2H, m, $-\text{CH}_2-$), 1.25 (29H, t, $J = 17.3$ Hz, $-\text{CH}_2-$ and $-\text{CH}_3$), 0.87 (3H, t, $J = 6.6$ Hz, $-\text{CH}_3$), 0.62 (3H, s, $-\text{CH}_3$).

^{13}C NMR (CDCl_3 , 101 MHz) δ (ppm): 147.93, 133.93, 132.73, 132.31, 116.46, 115.59, 115.47, 115.22, 100.67, 72.01, 44.13, 32.06, 30.23, 29.83, 29.82, 29.79, 29.76, 29.73, 29.69, 29.68, 29.61, 29.49, 22.90, 22.84, 22.83, 21.97, 14.26.

Elemental analysis: calcd. (%) for $\text{C}_{29}\text{H}_{44}\text{O}_2\text{N}_2$: C, 76.95; H, 9.80; N, 6.19; found: C, 75.79; H, 9.62; N, 6.23. The rather large deviation of the carbon content from the theoretical value is probably due to traces of toluene, the recrystallization solvent. However the ^1H - and ^{13}C -NMR spectra shown on page S25 prove the high purity of the compound.

ESI-HR-MS: $[\text{M}+\text{NH}_4]^+ = 470.3739$; calcd. for $[\text{M} = \text{C}_{29}\text{H}_{48}\text{N}_3\text{O}_2]^+ = 470.3741$

Synthesis of 4-(2,5,5-trimethyl-1,3-dioxan-2-yl)phthalonitrile (4a):

Using the above procedure, the compound **4a** was obtained from 2-(3,4-dichlorophenyl)-2,5,5-trimethyl-1,3-dioxane **3a** (2.0 g, 7.27 mmol), tris(dibenzylideneacetone)-dipalladium(0) ($\text{Pd}_2(\text{dba})_3$) (0.53 g, 0.58 mmol), 1,1'-bis(diphenyl-phosphino)ferrocene (DPPF) (0.64 g, 1.16 mmol), active zinc (0.23 g, 3.48 mmol), zinc cyanide (1.36 g, 11.63 mmol). $R_f = 0.36$ (ethyl acetate:*n*-hexane, v:v = 1:2). Yield: 1.37 g, 74%.

^1H NMR (CDCl_3 , 400MHz) δ (ppm): 7.89 (1H, d, $J = 0.7$ Hz, 1H, ArH), 7.85 (1H, d, $J = 8.1$ Hz, ArH), 7.81 (1H, dd, $J = 8.2, 1.3$ Hz, ArH), 3.48 (2H, d, $J = 11.2$ Hz, $-\text{CH}_2-$), 3.23 (2H, d, $J = 11.0$ Hz, $-\text{CH}_2-$), 1.52 (3H, s, $-\text{CH}_3$), 1.24 (3H, s, $-\text{CH}_3$), 0.64 (3H, s, $-\text{CH}_3$).

^{13}C NMR (CDCl_3 , 101 MHz) δ (ppm): 148.64, 134.17, 132.18, 131.73, 116.65, 115.52, 115.43, 115.31, 99.06, 72.10, 31.20, 30.15, 22.69, 21.95.

Elemental analysis: calcd. (%) for $\text{C}_{15}\text{H}_{16}\text{O}_2\text{N}_2$: C, 70.29; H, 6.29; N, 10.93, found: C, 70.55; H, 6.28; N, 10.83.

ESI-HR-MS: $[\text{M} + \text{NH}_4]^+ = 274.1550$; calcd. for $[\text{M} = \text{C}_{15}\text{H}_{20}\text{N}_3\text{O}_2]^+ = 274.1550$

Synthesis of 4-(5,5-dimethyl-2-pentyl-1,3-dioxan-2-yl)phthalonitrile (4b):

For the compound **4b**, the procedure was similar with the above one using 2-(3,4-dichlorophenyl)-5,5-dimethyl-2-pentyl-1,3-dioxane **3b** (2.0 g, 6.04 mmol), tris(dibenzylideneacetone)-dipalladium(0) ($\text{Pd}_2(\text{dba})_3$) (0.44 g, 0.48 mmol), 1,1'-bis(diphenyl-phosphino)ferrocene (DPPF) (0.54 g, 0.97 mmol), active zinc (0.19 g, 2.90 mmol), zinc cyanide (1.13 g, 9.66 mmol). $R_f = 0.38$ (ethyl acetate:*n*-hexane, v:v = 1:4). Yield: 0.72 g, 38%.

^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 7.84 (2H, dd, $J = 4.7, 3.3$ Hz, ArH), 7.76 (1H, dd, $J = 8.2, 1.5$ Hz, ArH), 3.46 (2H, d, $J = 11.2$ Hz, $-\text{CH}_2-$), 3.21 (2H, d, $J = 11.0$ Hz, $-\text{CH}_2-$), 1.73-1.63 (2H, m, $-\text{CH}_2-$), 1.38-1.12 (9H, m, $-\text{CH}_2-$ and $-\text{CH}_3$), 0.83 (3H, t, $J = 7.0$ Hz, $-\text{CH}_3$), 0.61 (3H, s, $-\text{CH}_3$).

^{13}C NMR (CDCl_3 , 101 MHz) δ (ppm): 147.90, 133.94, 132.70, 132.31, 116.40, 115.58, 115.47, 115.17, 100.32, 71.98, 43.89, 31.67, 30.10, 22.81, 22.60, 22.51, 21.93, 14.09.

Elemental analysis: calcd. (%) for $\text{C}_{19}\text{H}_{24}\text{O}_2\text{N}_2$: C, 73.05; H, 7.74; N, 8.97, found: C, 73.57; H, 7.92; N, 9.12.

ESI-HR-MS: $[\text{M} + \text{NH}_4]^+ = 330.2174$; calcd. for $[\text{M} = \text{C}_{19}\text{H}_{28}\text{N}_3\text{O}_2]^+ = 330.2176$.

Synthesis of 4-(5,5-dimethyl-2-undecyl-1,3-dioxan-2-yl)phthalonitrile (4c):

Using 2-(3,4-dichlorophenyl)-5,5-dimethyl-2-undecyl-1,3-dioxane **3c** (2.0 g, 7.82 mmol), tris(dibenzylideneacetone)-dipalladium(0) ($\text{Pd}_2(\text{dba})_3$) (0.35 g, 0.39 mmol), 1,1'-bis(diphenylphosphino)ferrocene (DPPF) (0.43 g, 0.77 mmol), active zinc (0.15 g, 2.31 mmol), zinc cyanide (0.90 g, 7.71 mmol), compound **4c** was obtained as a white powder. $R_f = 0.37$ (ethyl acetate:*n*-hexane, v:v = 1:4). Yield: 1.70 g, 85%.

$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ (ppm): 7.84 (2H, dd, $J = 4.7, 3.1\text{ Hz}$, ArH), 7.76 (1H, dd, $J = 8.2, 1.6\text{ Hz}$, ArH), 3.46 (2H, d, $J = 11.3\text{ Hz}$, $-\text{CH}_2-$), 3.21 (2H, d, $J = 11.0\text{ Hz}$, $-\text{CH}_2-$), 1.72-1.63 (2H, m, $-\text{CH}_2-$), 1.38-1.11 (21H, m, $-\text{CH}_2-$ and $-\text{CH}_3$), 0.91-0.77 (3H, m, $-\text{CH}_3$), 0.61 (3H, s, $-\text{CH}_3$).

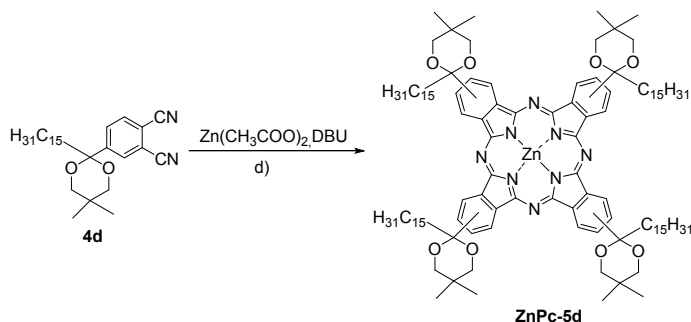
$^{13}\text{C NMR}$ (CDCl_3 , 101 MHz) δ (ppm): 147.91, 133.93, 132.71, 132.31, 116.42, 115.58, 115.46, 115.18, 100.65, 71.99, 44.11, 32.01, 30.21, 29.70, 29.68, 29.65, 29.58, 29.43, 22.87, 22.82, 22.79, 21.94, 14.23.

Elemental analysis: calcd (%) for $\text{C}_{25}\text{H}_{36}\text{O}_2\text{N}_2$: C, 75.72; H, 9.15; N, 7.06, found: C, 76.27; H, 9.28; N, 7.09.

ESI-HR-MS: $[\text{M}+\text{NH}_4]^+ = 414.3113$; calcd. for $[\text{M} = \text{C}_{25}\text{H}_{40}\text{N}_3\text{O}_2]^+ = 414.3115$.

General procedure for the synthesis of the substituted phthalocyaninatozinc(II) compounds:

Synthesis of 2(3), 9(10), 16(17), 23(24)-tetrakis[(5,5-dimethyl-2-pentadecyl-1,3-dioxan-2-yl)phthalocyaninato]zinc(II) (ZnPc-5d):



In a dry 250 mL three-neck flask equipped with a thermometer, reflux condenser, were added under argon 2-(3,4-dichlorophenyl)-5,5-dimethyl-2-pentadecyl-1,3-dioxan-2-yl (**4d**, 0.90 g, 1.99 mmol), 150 mL of 1-pentanol and 1,8-diazabicyclo[5.4.0]undec-7-ene (0.76 g, 4.98 mmol). This reaction mixture was purged with argon for 10 minutes. Thereafter the reaction mixture was heated to 130 °C, and zinc acetate (0.23 g, 1.26 mmol) was added and then heated further to reflux for 48 hours. The color changed to turquoise. The 1-pentanol was distilled off under reduced pressure. The residue was dissolved in dichloromethane, and washed with saturated ammonium chloride solution, saturated sodium chloride solution and then with water. The product was dried over sodium sulfate and the solvent was vaporized to leave a turquoise residue. This was followed by chromatography using a column (length = 30 cm, diameter = 3.5 cm) on silica gel with a mixture of ethyl acetate: *n*-hexane: 1:2 (v:v) as eluent. $R_f = 0.77$. Yield: 0.42 g, 45%.

UV-Vis: λ_{\max} (lg ϵ_{\max}), 678 (5.34), 649 (4.46), 611 (4.52), 344.5 (4.83).

MALDI-HR-MS: $M^{+\bullet} = 1873.2902$; calcd. for $[M = C_{116}H_{176}N_8O_4Zn]^{+\bullet} = 1873.2897$.

Synthesis of 2(3), 9(10), 16(17), 23(24)-tetrakis[(2,5,5-trimethyl-1,3-dioxan-2-yl)phthalocyaninato]zinc(II) (ZnPc-5a):

Using **4a** (0.81 g, 3.18 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (1.21 g, 7.95 mmol) and zinc acetate (0.36 g, 1.99 mmol), compound **ZnPc-5a** was afforded as a turquoise powder. $R_f = 0.52$ (ethyl acetate/*n*-hexane, v:v = 1:2). Yield: 0.65 g, 76 %.

UV-Vis: λ_{\max} (lg ϵ_{\max}), 677.5 (4.74), 648.5 (3.82), 611 (2.87), 344.5 (4.24).

HR-MS-ESI: $[M+H]^+ = 1089.4208$; calcd. for $[M = C_{60}H_{65}N_8O_8Zn]^+ = 1089.4211$.

Synthesis of 2(3), 9(10), 16(17), 23(24)-tetrakis[4-(5,5-dimethyl-2-pentyl-1,3-dioxan-2-yl)phthalocyaninato]zinc(II) (ZnPc-5b):

For the preparation of compound **ZnPc-5b**, **4b** (0.41 g, 1.30 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (0.50 g, 3.26 mmol) and zinc acetate (0.15 g, 0.81 mmol) were used. $R_f = 0.43$ (ethyl acetate/*n*-hexane, v:v = 1:5). Yield: 0.214 g, 54.18%.

UV-Vis: λ_{\max} (lg ϵ_{\max}), 676.5 (4.97), 648.5 (4.05), 609 (4.13), 344.5 (4.46).

HR-MS-ESI: $[M+H]^+ = 1313.6715$; calcd. for $[M = C_{76}H_{97}N_8O_8Zn]^+ = 1313.6715$.

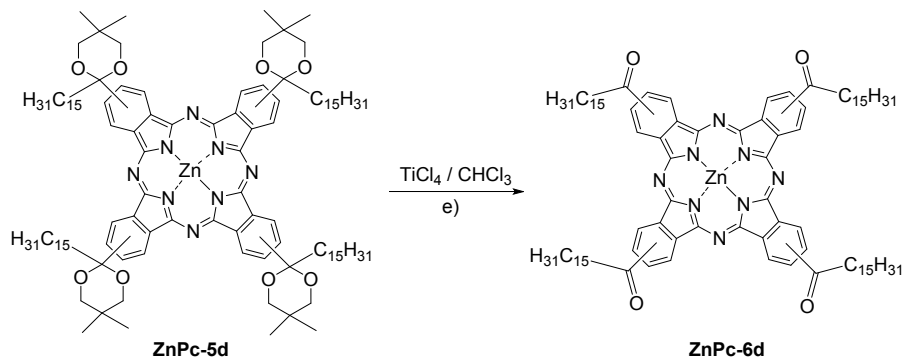
Synthesis of 2(3), 9(10), 16(17), 23(24)-tetrakis[4-(5,5-dimethyl-2-undecyl-1,3-dioxan-2-yl)phthalocyaninato]zinc(II) (ZnPc-5c):

Using **4c** (0.540 g, 1.36 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (0.52 g, 3.43 mmol) and zinc acetate (0.15 g, 0.84 mmol) the compound **ZnPc-5c** could be obtained in 26.0 % yield (0.143 g). $R_f = 0.45$ (ethyl acetate/*n*-hexane, v:v = 1:5)

UV-Vis: λ_{\max} (lg ϵ_{\max}), 677.5 (5.21), 649 (4.31), 611 (4.38), 344.5 (4.71).

HR-MS-ESI: $[M+H]^+ = 1652.0496$; calcd. For $[M = C_{100}H_{145}N_8O_8Zn]^+ = 1652.0492$.

Synthesis of 2(3), 9(10), 16(17), 23(24)-tetrapalmitoylphthalocyaninatozinc(II) (ZnPc-6d):



A solution of TiCl_4 in CHCl_3 (0.1 M, 3.0 mL, 0.3 mmol) was added dropwise by syringe, under argon, to a solution of **ZnPc-5d** (279 mg; 0.149 mmol) in dry CHCl_3 (5 mL). The reaction mixture was stirred at room temperature for 2 hours, hydrolyzed by addition of a saturated aqueous NaHCO_3 solution (20 mL) and left under stirring overnight. The crude reaction mixture was extracted with ethyl acetate, and the solvents were evaporated to dryness. This was followed by chromatography using a column (length = 30 cm, diameter = 3.5 cm) on silica gel with a mixture of ethyl acetate: *n*-hexane: 1:3 (v:v) as eluent. $R_f = 0.84$. Yield: 74 mg, 33%.

MALDI-HR-MS: $M^{+\bullet} = 1528.9957$; calcd. For $M^{+\bullet} = 1528.9970$.

Synthesis of 2(3), 9(10), 16(17), 23(24)-tetraacetylphthalocyaninatozinc(II) (ZnPc-6a):

A solution of TiCl_4 in CHCl_3 (0.1 M, 5.0 mL, 0.5 mmol), **ZnPc-5a** (268 mg, 0.246 mol), TiCl_4 in CHCl_3 (0.1 M, 5.0 mL, 0.50 mmol) were used to obtain compound **ZnPc-6a**. Yield: 111 mg, 61%.

ESI-HR-MS: $M^+ = 744.1216$; calcd. for $M^+ = 744.1206$.

Synthesis of 2(3), 9(10), 16(17), 23(24)-tetrahexanoylphthalocyaninatozinc(II) (ZnPc-6b):

Compound **ZnPc-6b** was prepared by the above procedure: a solution of TiCl_4 in CHCl_3 (0.1 M, 3.0 mL, 3.0 mmol), **ZnPc-5b** (180 mg, 0.137 mol). The compound was purified by column chromatography on silica gel, eluted with a mixture CH_2Cl_2 /ethyl acetate, 4:1 = v:v, then CH_2Cl_2 / CH_3OH , 10:1 = v:v. $R_f = 0.89$ (CH_2Cl_2 / CH_3OH , 10:1). Yield: 47 mg, 36 %.

ESI-HR-MS: $[M+CH_3COO]^- = 1027.3879$; calcd. for $[M+CH_3COO]^- = 1027.3855$.

Synthesis of 2(3), 9(10), 16(17), 23(24)-tetralauroylphthalocyaninatozinc(II) (ZnPc-6c):

For the preparation of the compound **ZnPc-6c**, the procedure was the same as for **ZnPc-6d**: a solution of $TiCl_4$ in $CHCl_3$ (0.1 M, 1.0 mL, 0.10 mmol), **ZnPc-5c** (70 mg, 0.04 mol). The compound **ZnPc-6c** was purified by column chromatography on silica gel using ethyl acetate/*n*-hexane, 1:3 = v:v, as eluent. $R_f = 0.76$ (ethyl acetate/*n*-hexane, 1:3). Yield: 28 mg, 53.6%.

MALDI-HR-MS: $M^{+\bullet} = 1304.7468$; calcd. for $M^{+\bullet} = 1304.7467$.

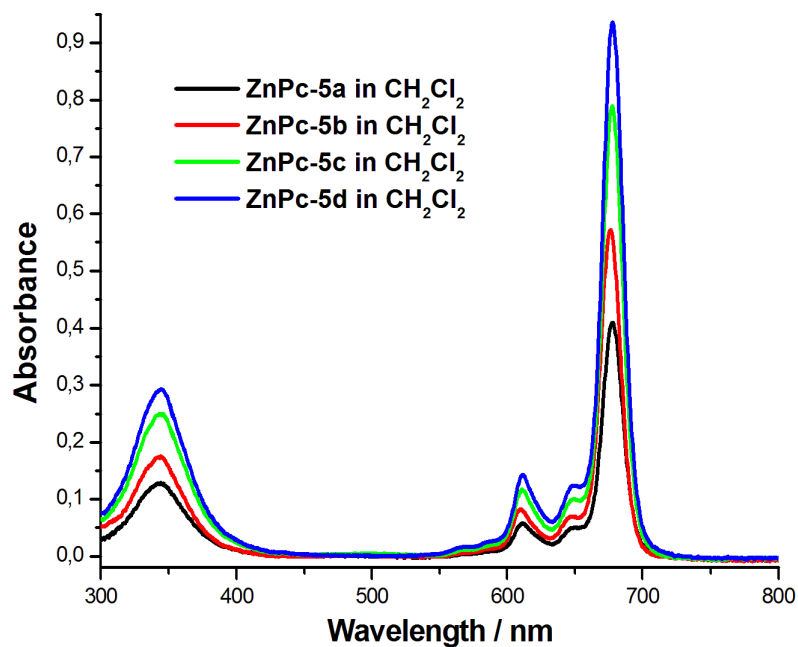


Figure S1. UV-Vis absorption spectra of tetra-carbonyl-protected **ZnPc-5a–d** (0.8 mg in 10 mL CH_2Cl_2).

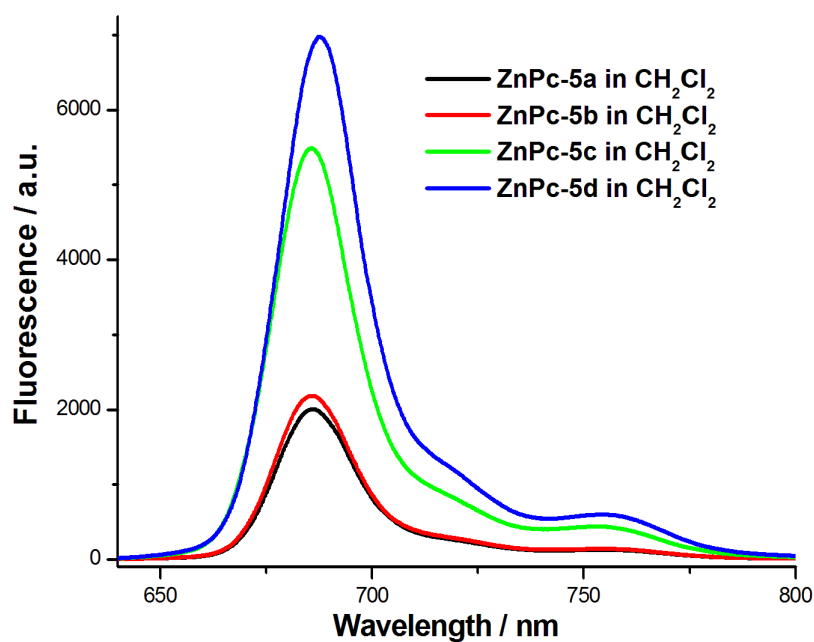


Figure S2. Fluorescence emission of tetra-carbonyl-protected **ZnPc-5a–d** excited at 350 nm (five drops of the corresponding solution used for above UV-Vis measurement were diluted to 1 mL).

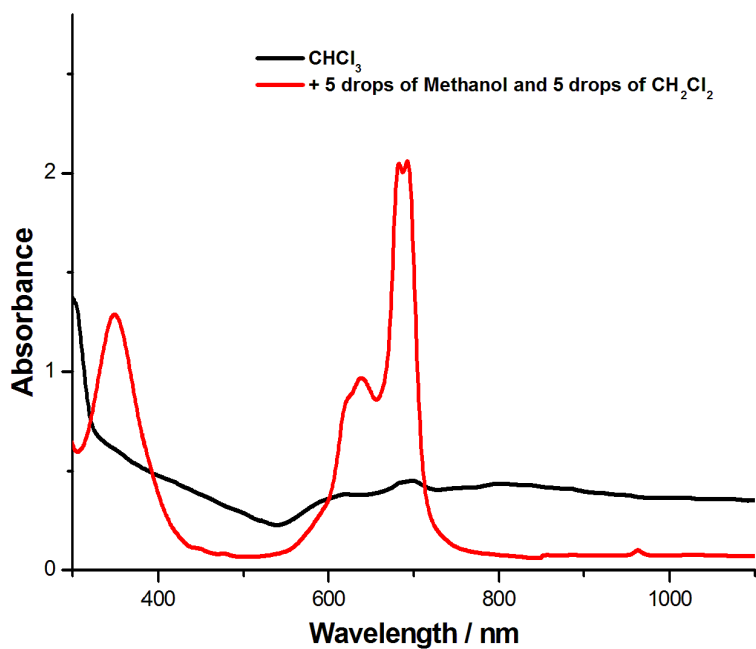


Figure S3. Absorption spectra of **ZnPc-6a** in dry CHCl₃ (black trace) and addition of five drops CH₃OH and five drops of CH₂Cl₂ (diluted 8 times, red trace).

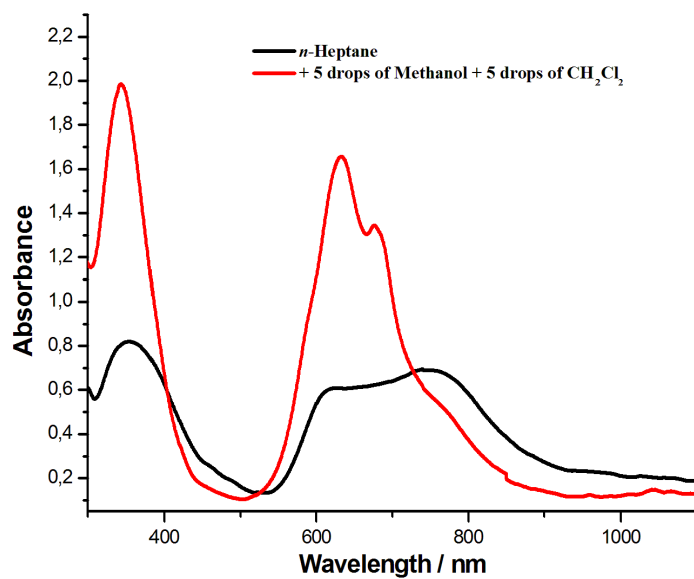


Figure S4. Absorption spectra of **ZnPc-6b** in dry *n*-heptane (black trace) and addition of five drops CH₃OH and five drops of CH₂Cl₂ (red trace).

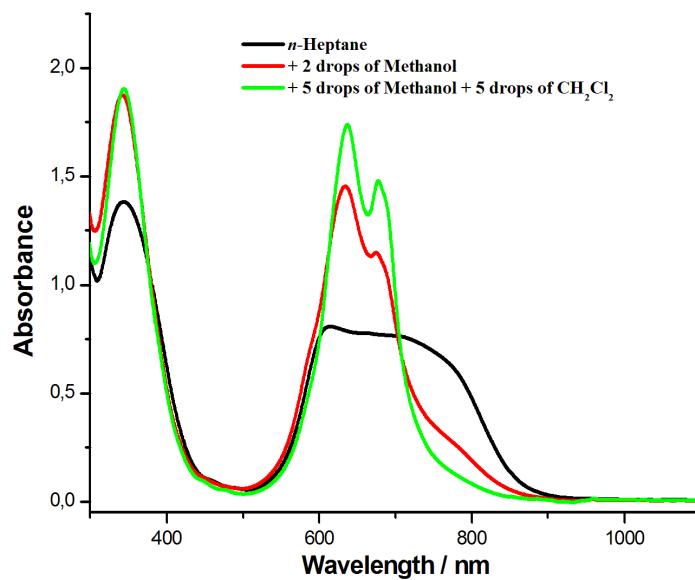


Figure S5. Absorption spectra of **ZnPc-6c** in dry *n*-heptane (black trace) and addition of two drops of methanol (red trace) following by five drops of CH₃OH and five drops of CH₂Cl₂ (green trace).

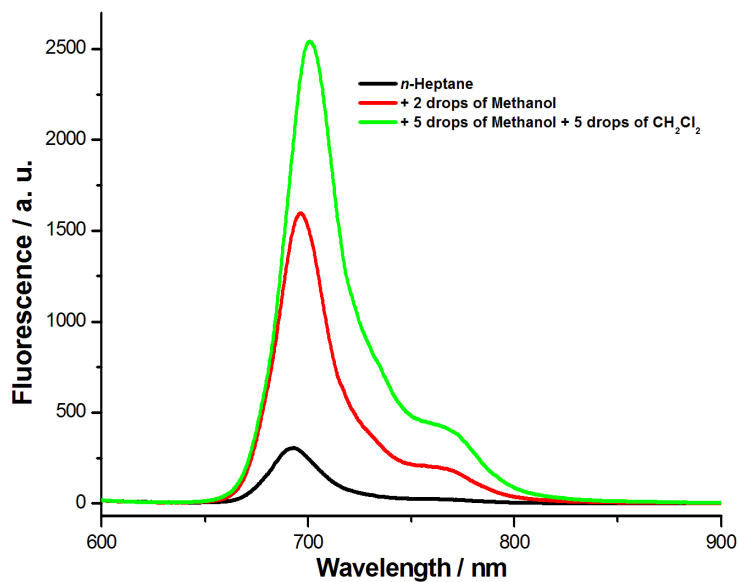


Figure S6. Gradual enhanced fluorescence emission of **ZnPc-6d** during the disassembly process. In dry *n*-heptane (black trace), addition of two drops of CH₃OH (red trace) and followed by addition of five drops CH₃OH and five drops of CH₂Cl₂ (green trace).

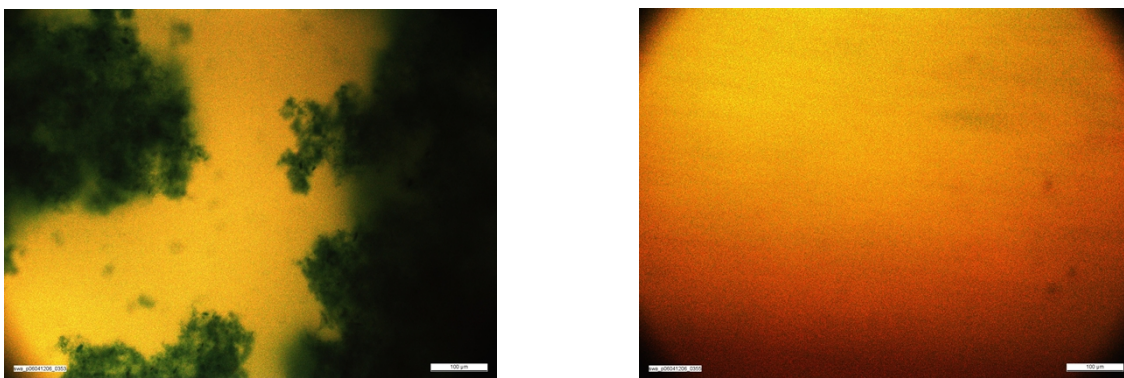


Figure S7. Fluffs of a dilauroyl ZnPc in dry *n*-heptane after standing for 30 min (left) and their disappearance after short sonication (right). The images were taken on Leica microscope. The white scale bar at right represents 100 μm . We thank Stefan Walheim (Karlsruhe Institute of Technology, INT) for their recording.

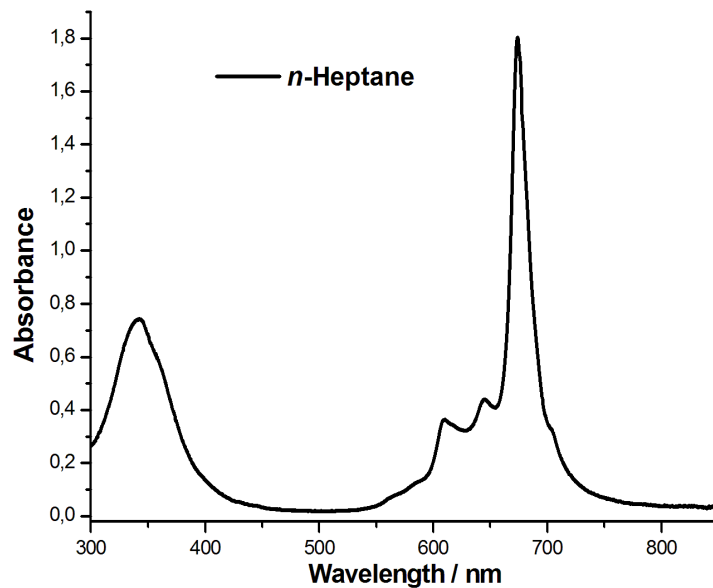


Figure S8. UV-Vis absorption spectra of tetrapalmitoyl-protected **ZnPc-5d** in *n*-heptane which could not self-assemble in a similar way as tetrapalmitoyl **ZnPc-6d**.

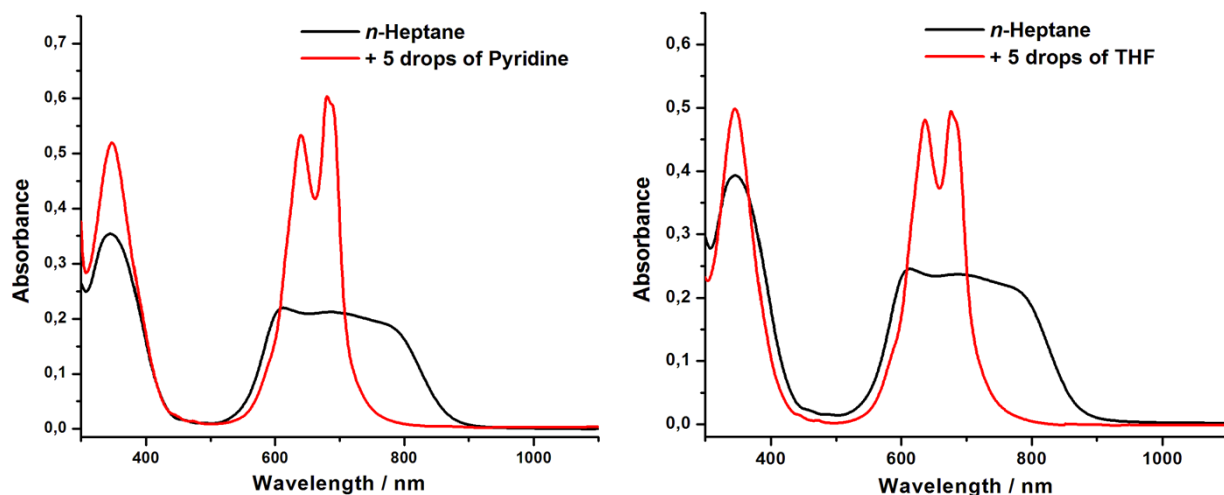


Figure S9. Absorption spectra of **ZnPc-6d** in dry *n*-heptane. At left, 3.3×10^{-5} M (black trace) and after addition of five drops of pyridine (red trace). At right, 4.0×10^{-5} M (black trace) and addition of and five drops of THF (red trace).

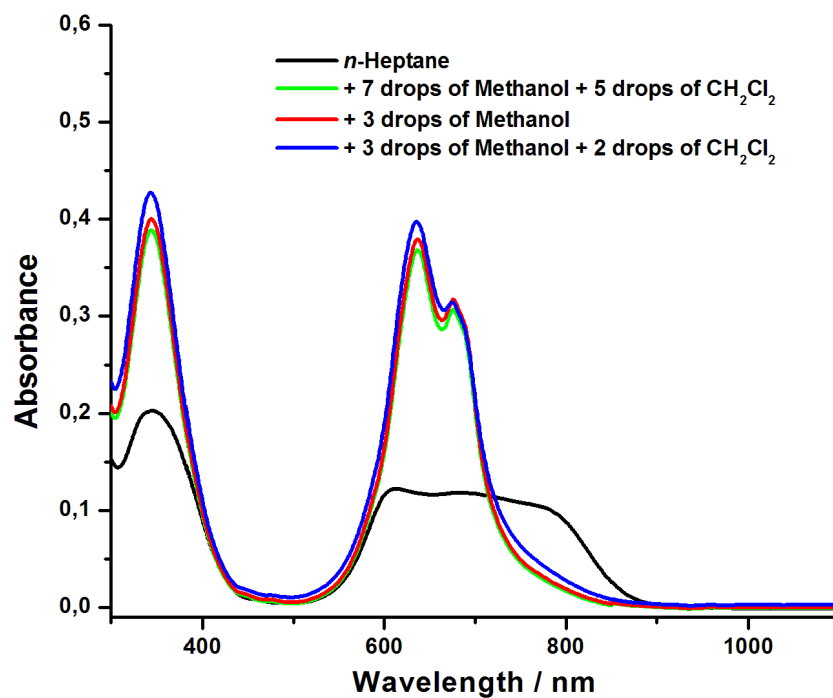


Figure S10. Absorption spectra of **ZnPc-6d** in dry *n*-heptane (2.0×10^{-5} M, black trace) and after sequential addition of three drops of methanol and 2 drops of CH_2Cl_2 (blue trace); three drops of methanol (red trace); and seven drops of methanol and five drops of CH_2Cl_2 (green trace).

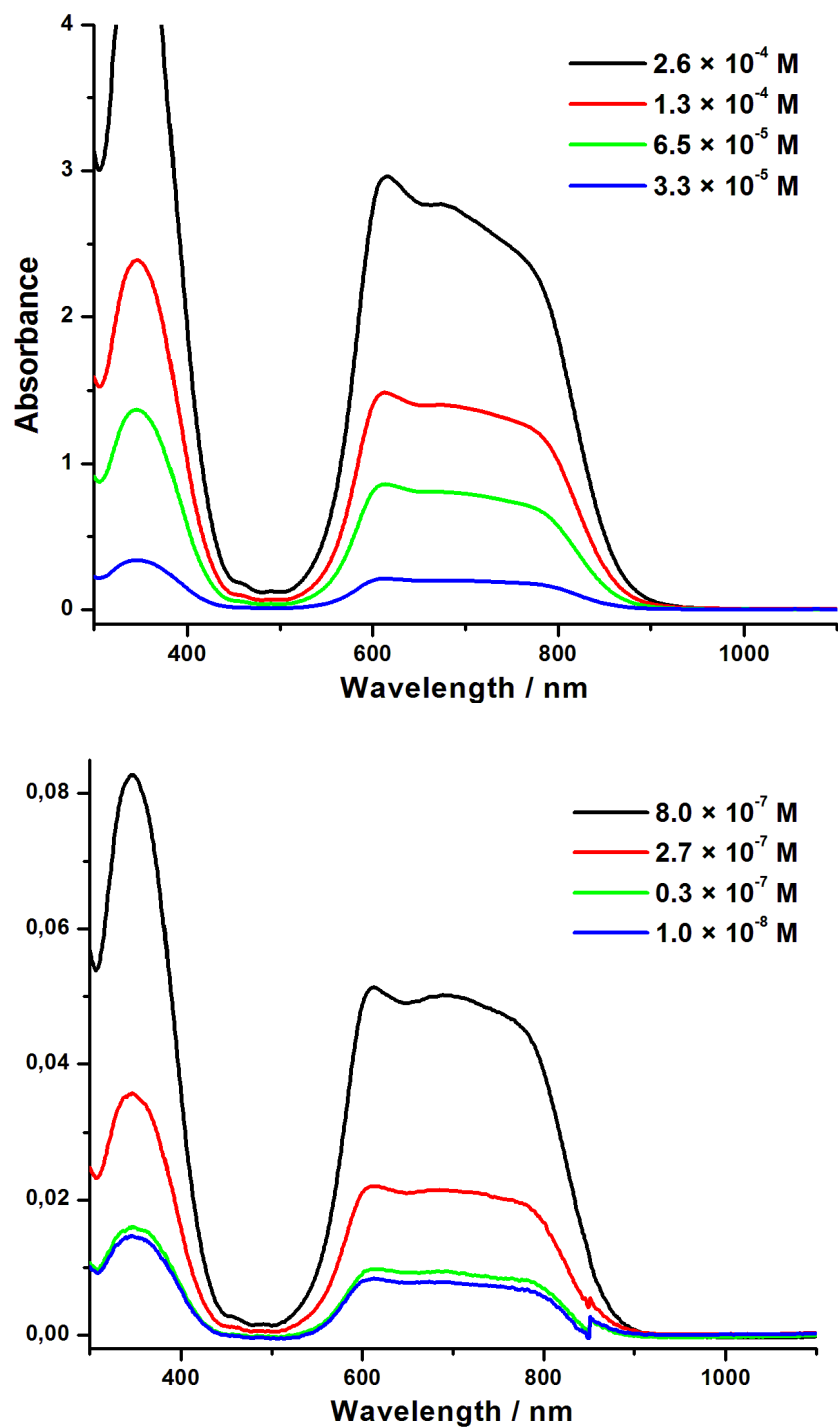


Figure S11. Concentration-dependent absorption spectra of **ZnPc-6d** in dry *n*-heptane (the top traces were recorded in with a 1 mm pathlength quartz cuvette, while the bottom traces were recorded in a 10 mm quartz cuvette. The jump around 850 nm in the bottom traces are due to the change of the detector). These experiments show that unlike similar self-assembling porphyrins, the phthalocyanines are more prone to self-assemble even at very dilute concentrations.

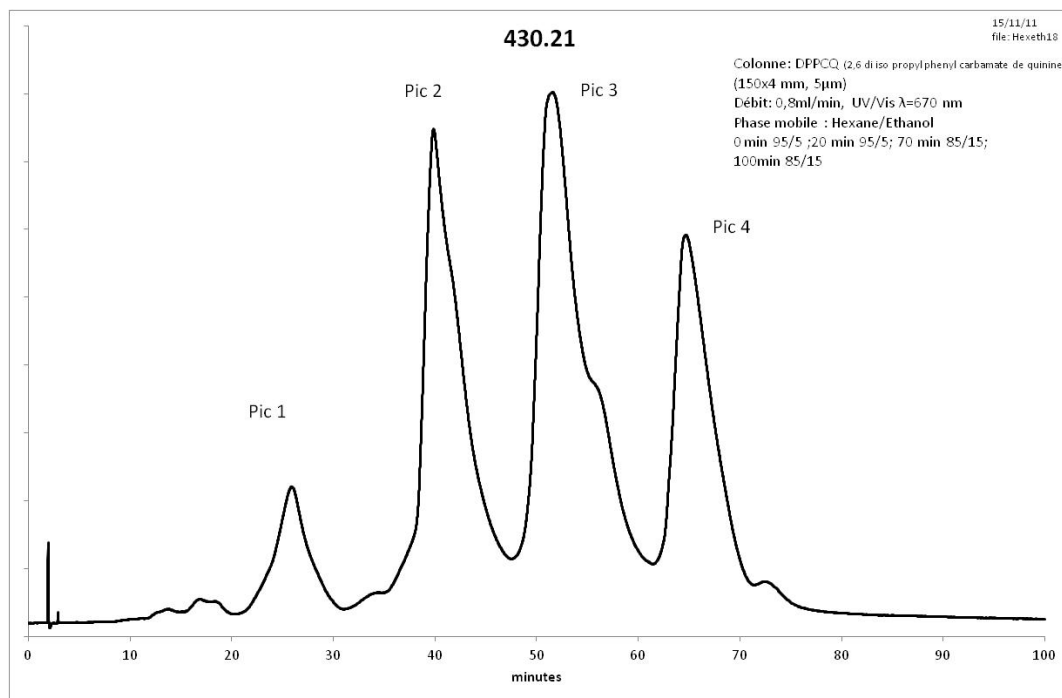


Figure S12. HPLC-Trace of a tetralauroyl-ZnPc separated on a 150×4 mm column filled with a bonded carbamate of 2,6-di-isopropylphenylquinine ($5 \mu\text{m}$ particles) eluted with 0.8 mL/min *n*-hexane / ethanol. The concentration gradient was 95/5 at 0 to 20 min and 85/15 at 70 to 100 min.

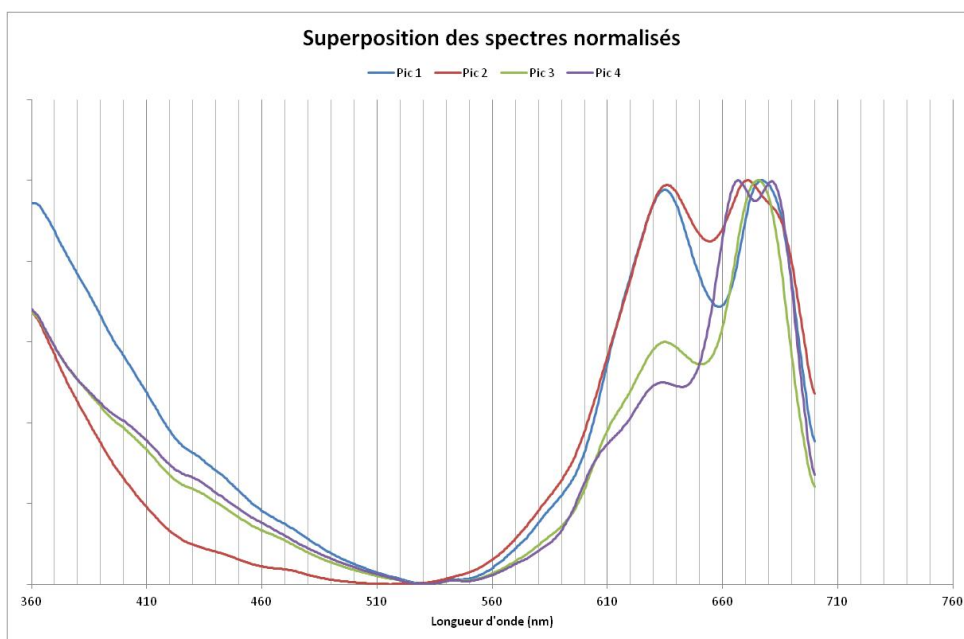


Figure S13. Normalized UV-Vis absorption spectra of the separated four peaks from the above HPLC run. The on-line detector cut-off is at 700 nm .

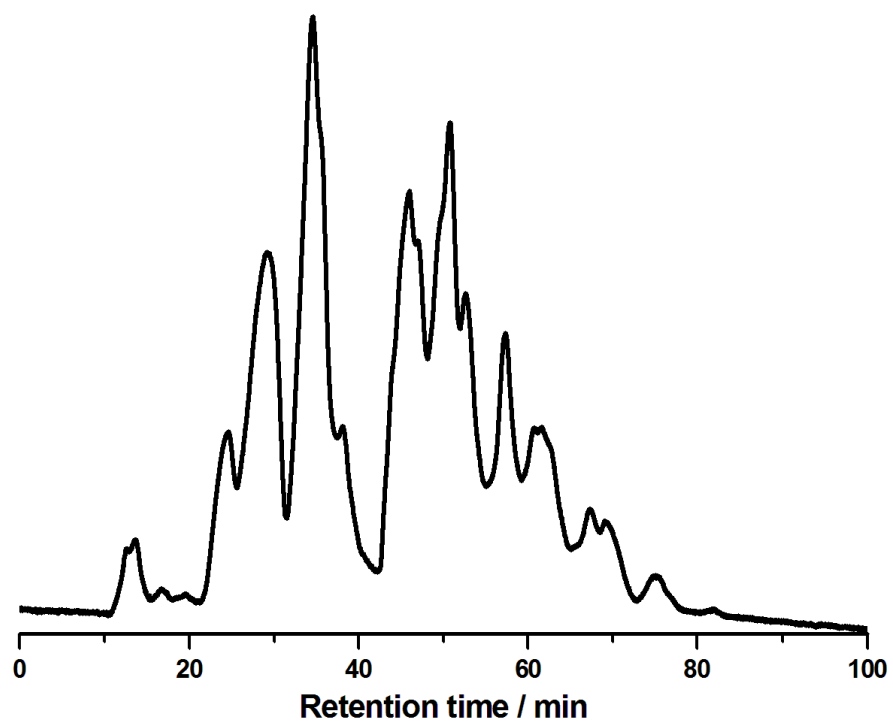


Figure S14. HPLC-Trace of a mixed condensation between 4-lauroyl-1,2-dicyanobenzene and the unsubstituted phthalodinitrile separated on a 150×4 mm column filled with a bonded carbamate of 2,6-di-isopropylphenylquinine ($5 \mu\text{m}$ particles) eluted with 0.8 mL/min *n*-hexane / ethanol. The concentration gradient was 95/5 at 0 to 70 min and 85/15 from 70 to 100 min.

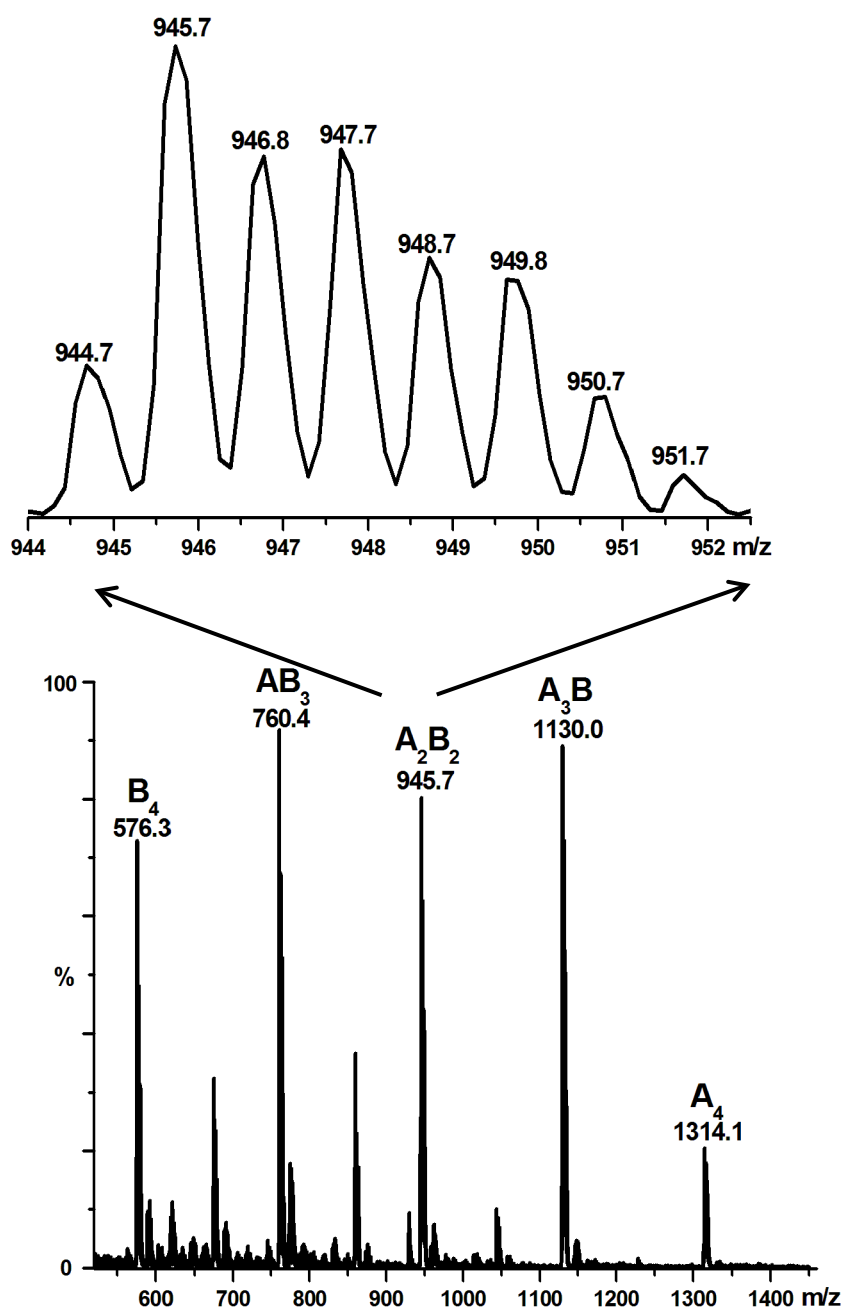
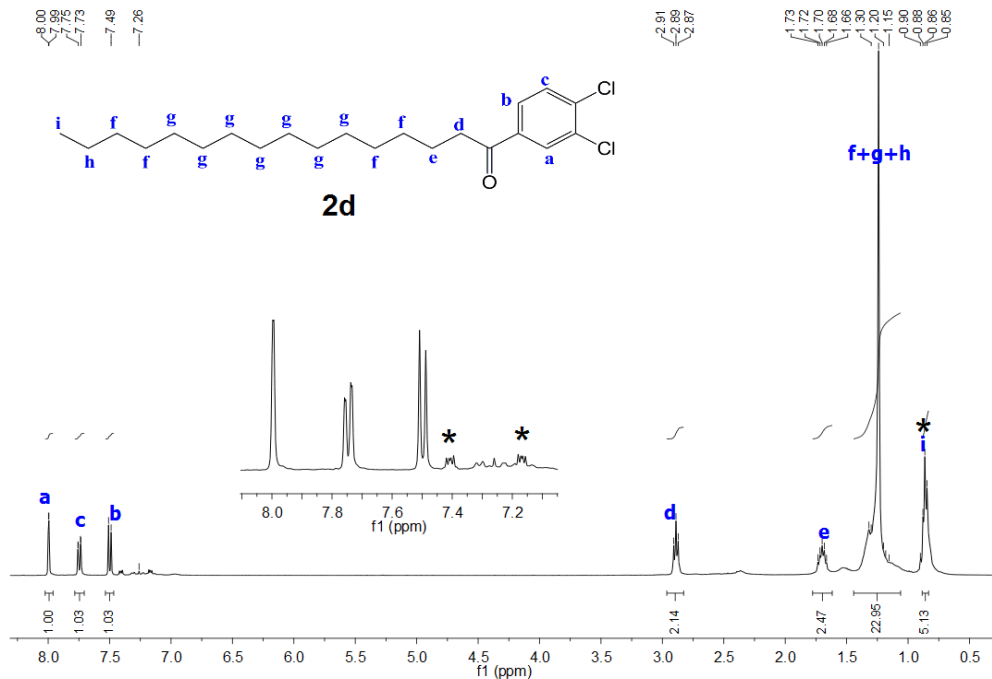
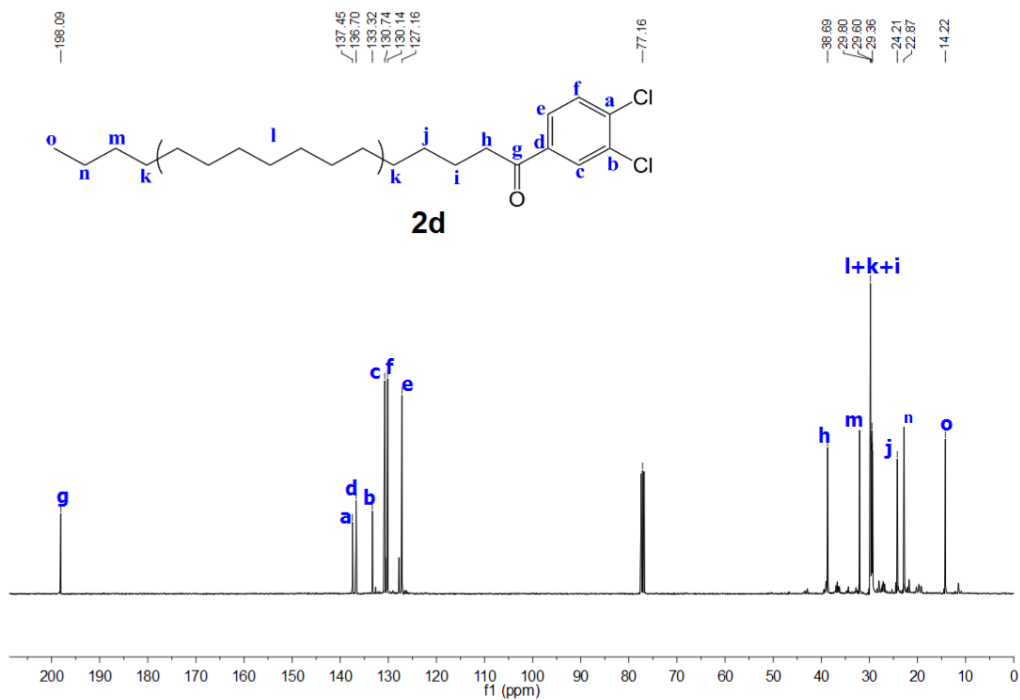


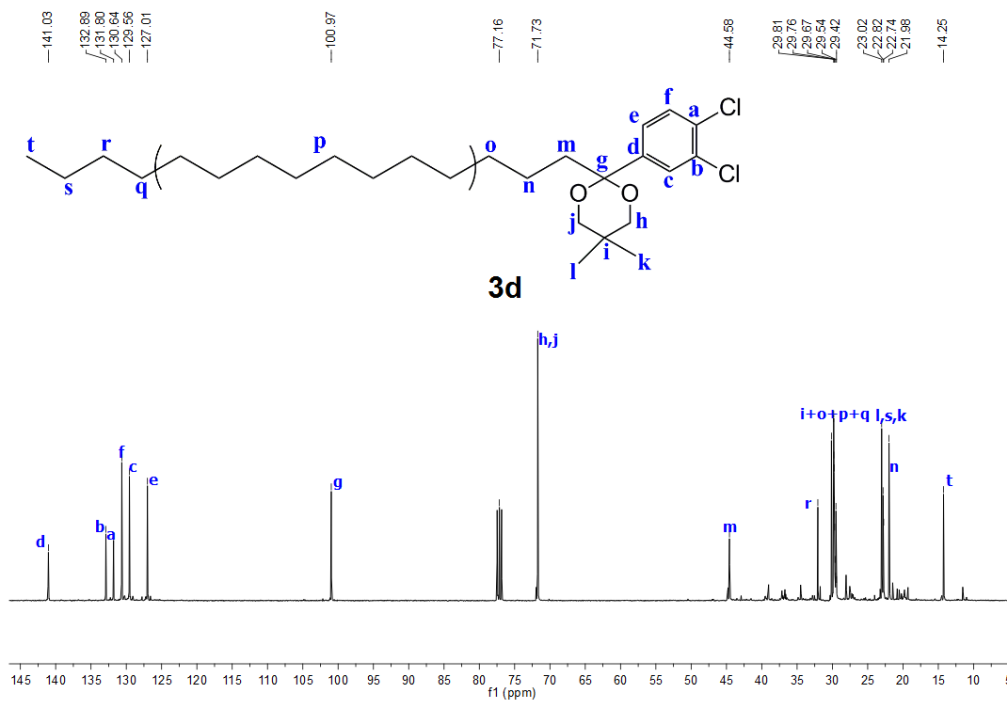
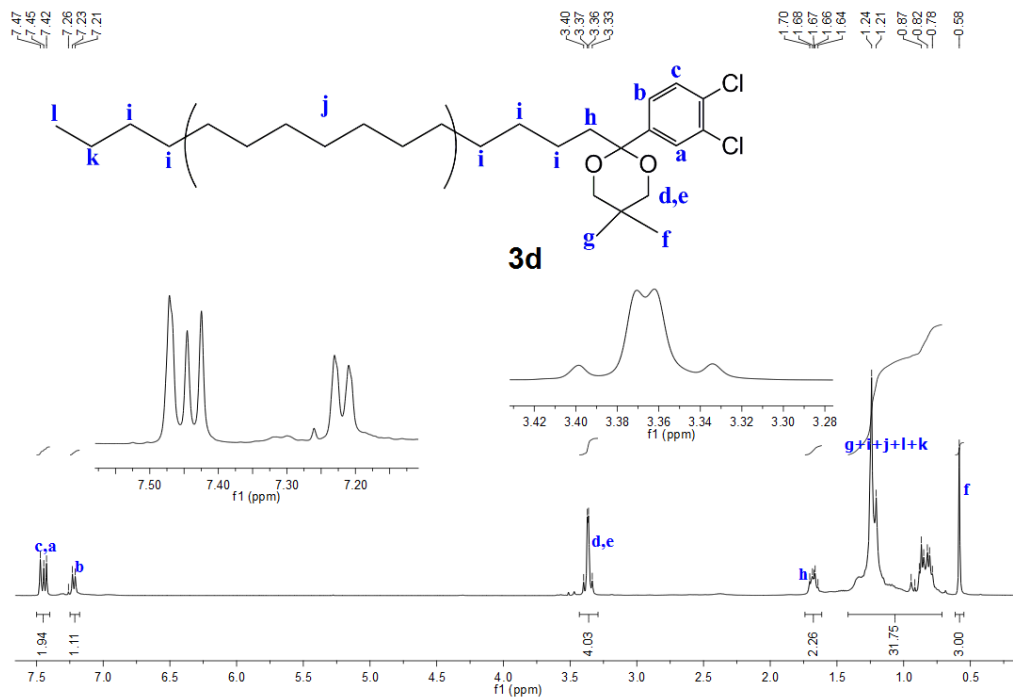
Figure S15. Example of an ESI-MS spectrum with an enlargement of the A_2B_2 peak of the mixed condensation of **4b** with the unsubstituted phthalodinitrile. Non-labeled peaks are fragment peaks.

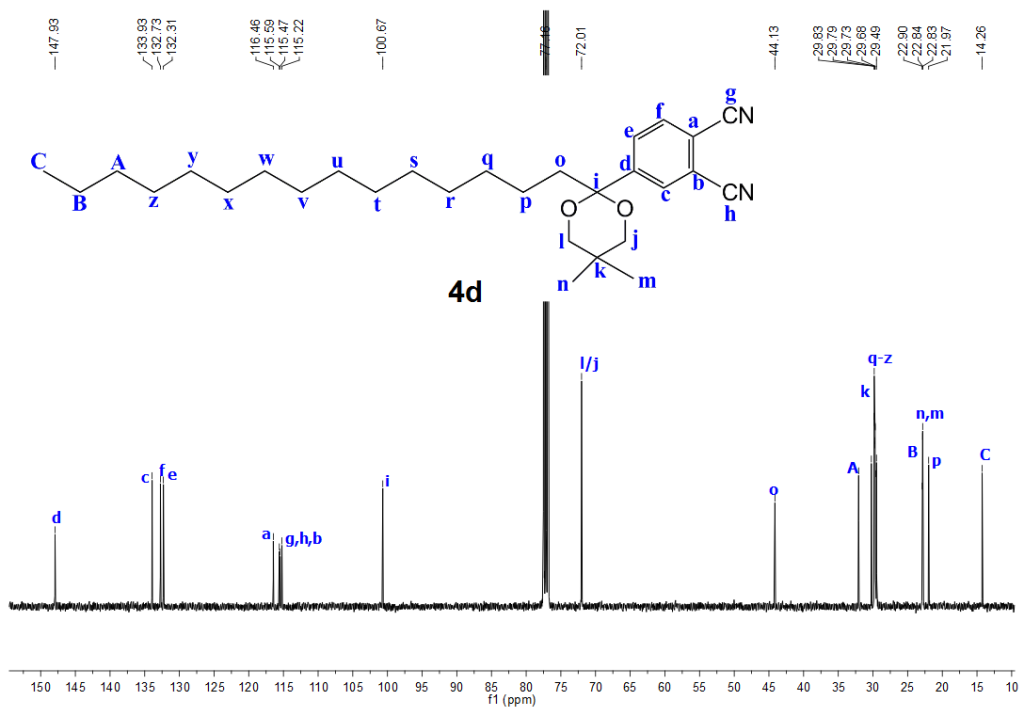
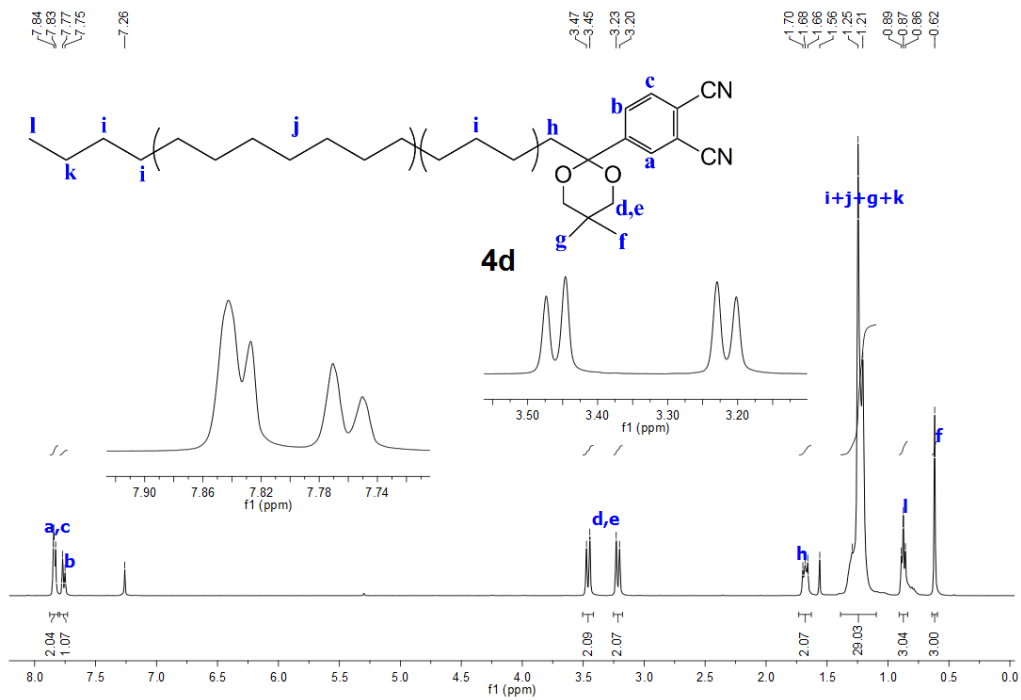
3. Typical ^1H / ^{13}C NMR Spectra in CDCl_3 and High-Resolution Mass Spectra



Peaks denoted by an asterisk are due to impurities (a phthalate ester).



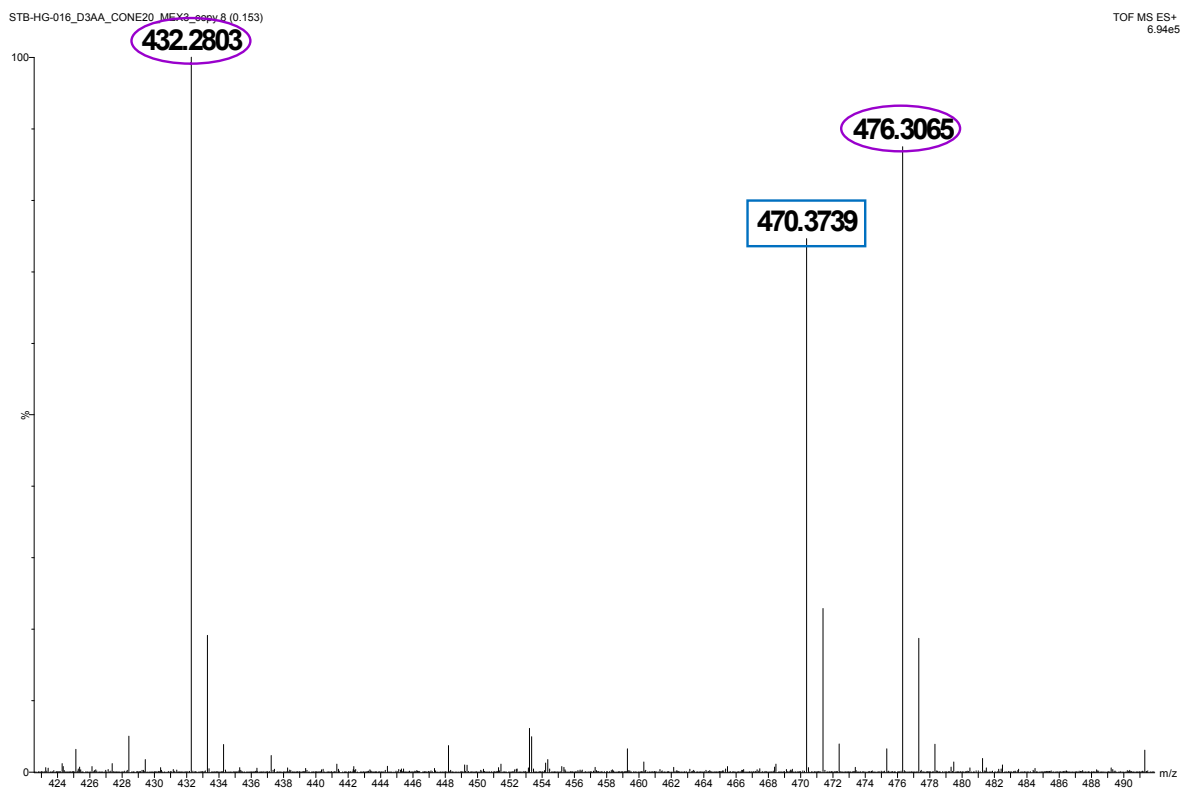




		m/z	error (mDa)	error (ppm)
Calculated value		470.3741	-	-
Experiment values	1	470.3736	- 0.5	- 1.1
	2	470.3735	- 0.6	- 1.3
	3	470.3739	- 0.2	- 0.4

These experimental determined values are associated with an ion of elementary composition $C_{29}H_{48}N_3O_2^+$.

HR-MS measurements by electrospray ionization in positive mode putting into evidence the ion $[M+NH_4]^+$ from the sample.

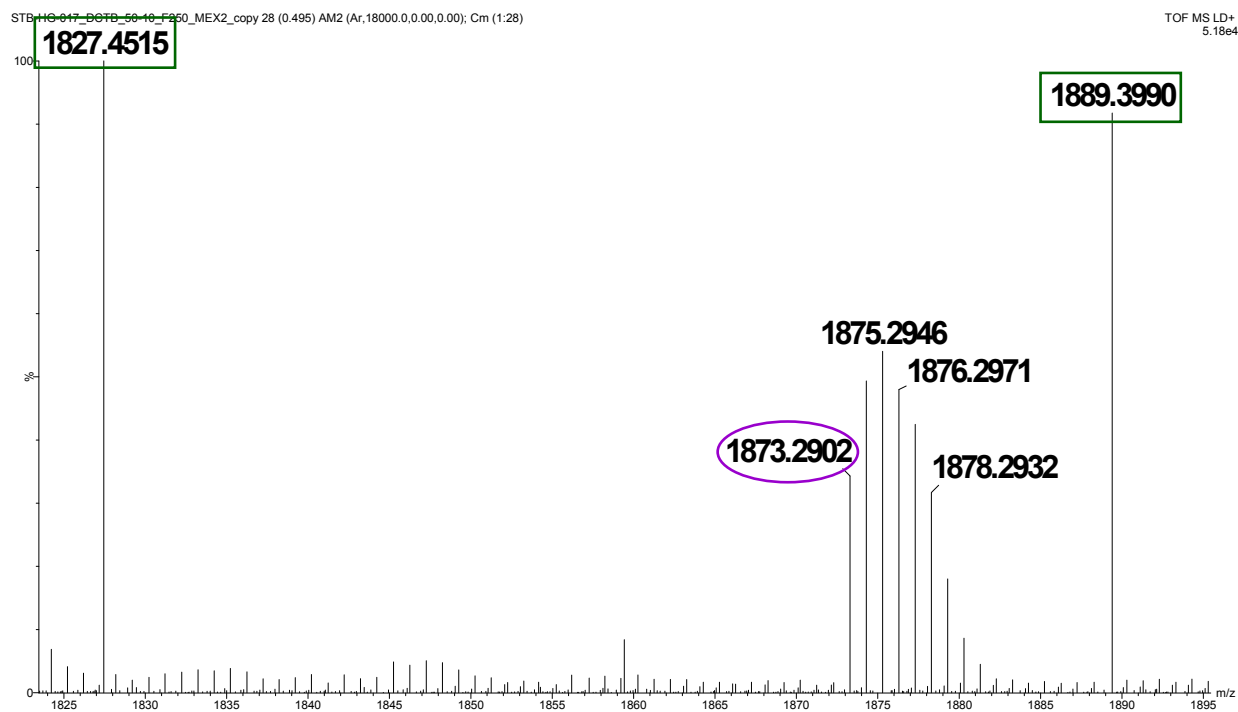


High Resolution Mass Spectrum in the positive mode of electrospray ionization of the sample **4d**. The targeted ion is detected at m/z 470.3739 (blue rectangle) while the peaks retained for internal calibration are observed at m/z 432.2803 and m/z 476.3065 (violet ellipses).

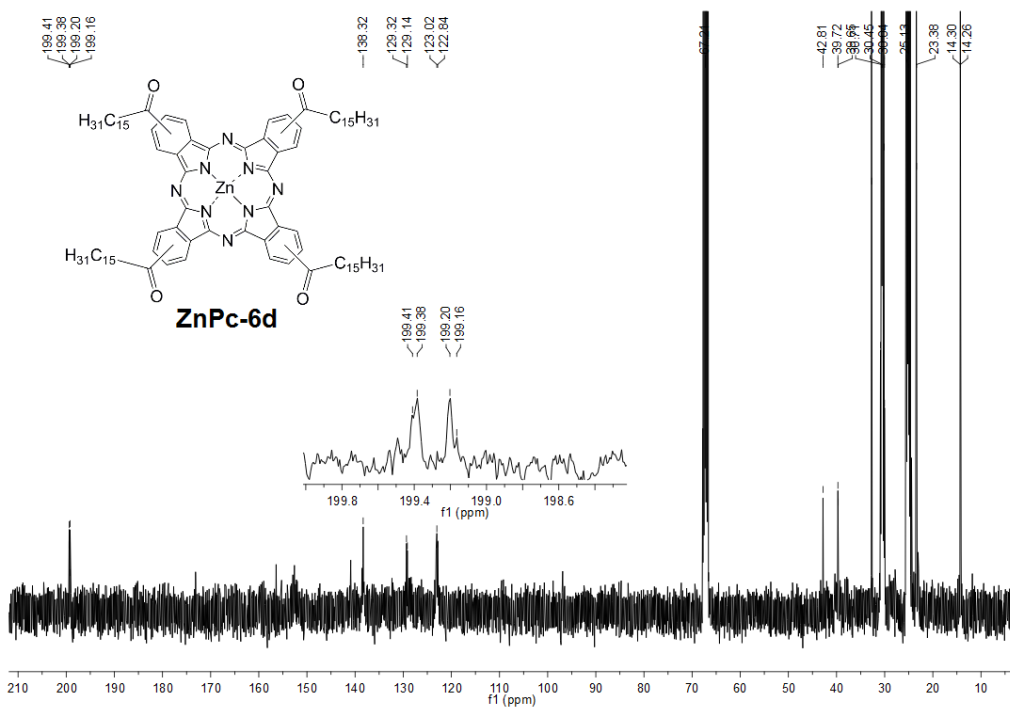
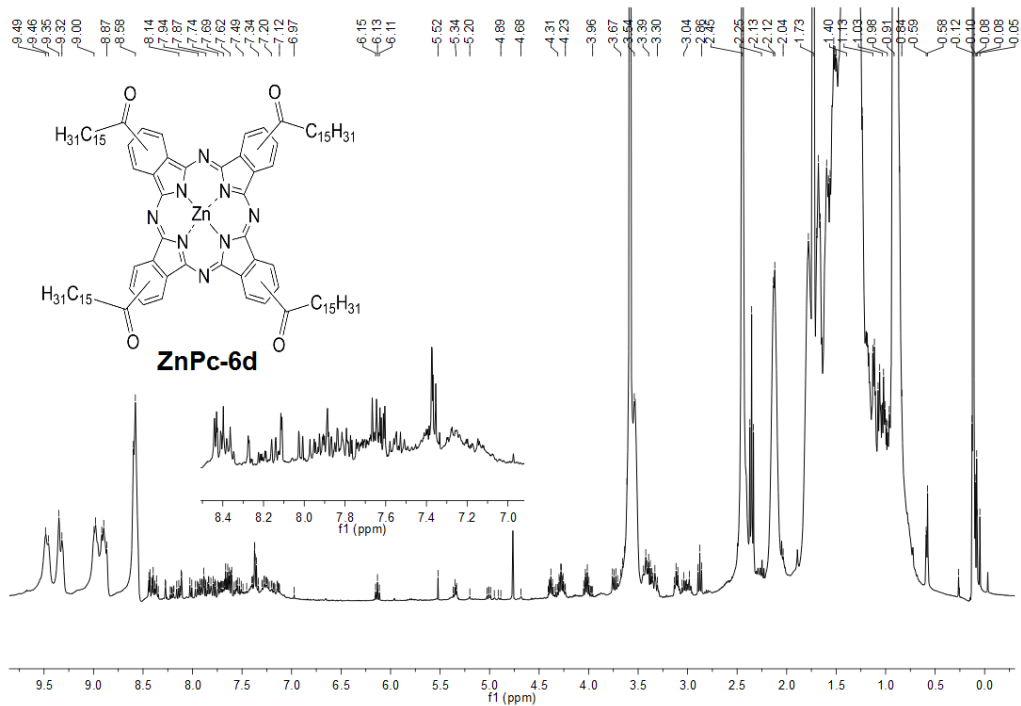
		m/z	error(mDa)	error (ppm)
Calculated value		1873.2897	-	-
Experiment values	1	1873.2904	+ 0.7	+ 0.4
	2	1873.2902	+ 0.5	+ 0.3
	3	1873.2915	+ 1.8	+ 1.0

These experimental determined values are associated with an ion of elementary composition $C_{116}H_{176}N_8O_8Zn^{+\bullet}$.

HR-MS measurements by MALDI putting into evidence the ion $M^{+\bullet}$ from the sample.



High Resolution Mass Spectrum in the $M^{+\bullet}$ mode of MALDI of the sample **ZnPc-5d**. The targeted ion is detected at m/z 1873.2902 (violet ellipse) while the peaks retained for internal calibration are observed at m/z 1827.4515 and m/z 1889.3990 (green rectangles).

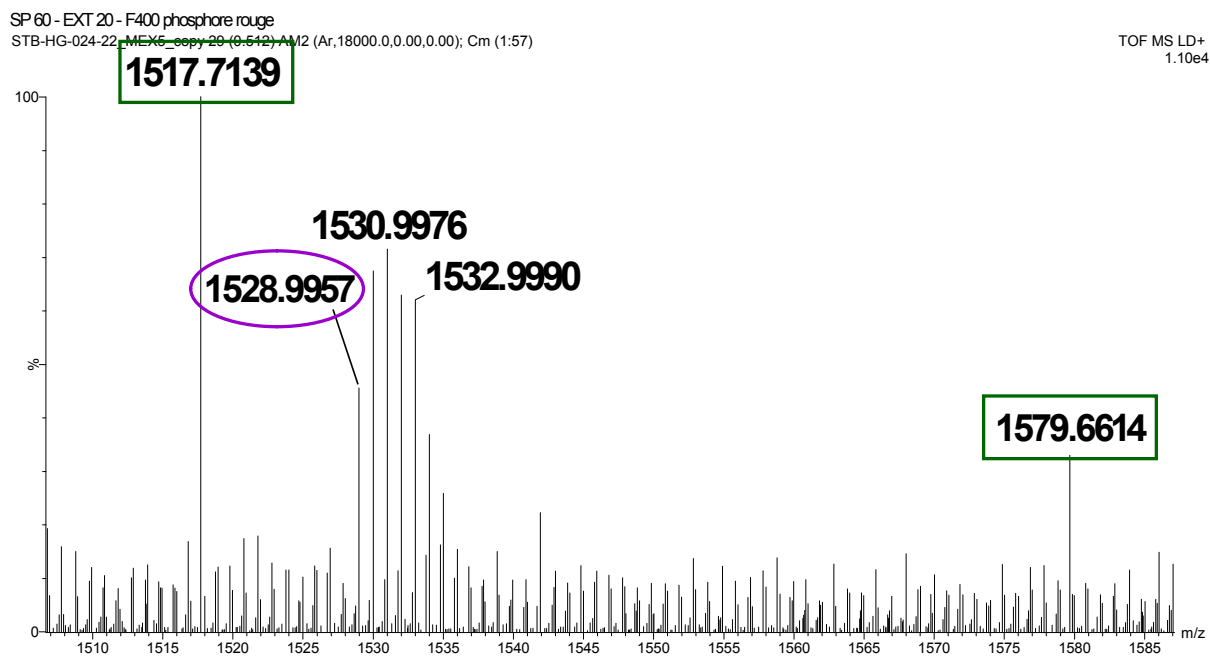


The ¹H/¹³C NMR of **ZnPc-6d** was recorded in THF-*d*₈.

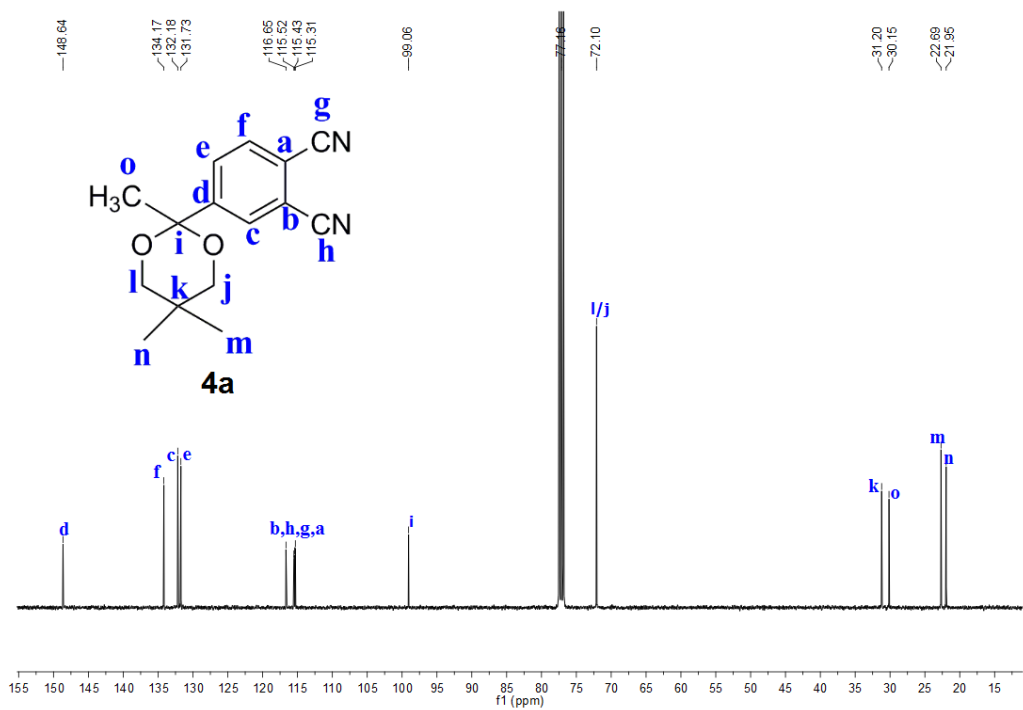
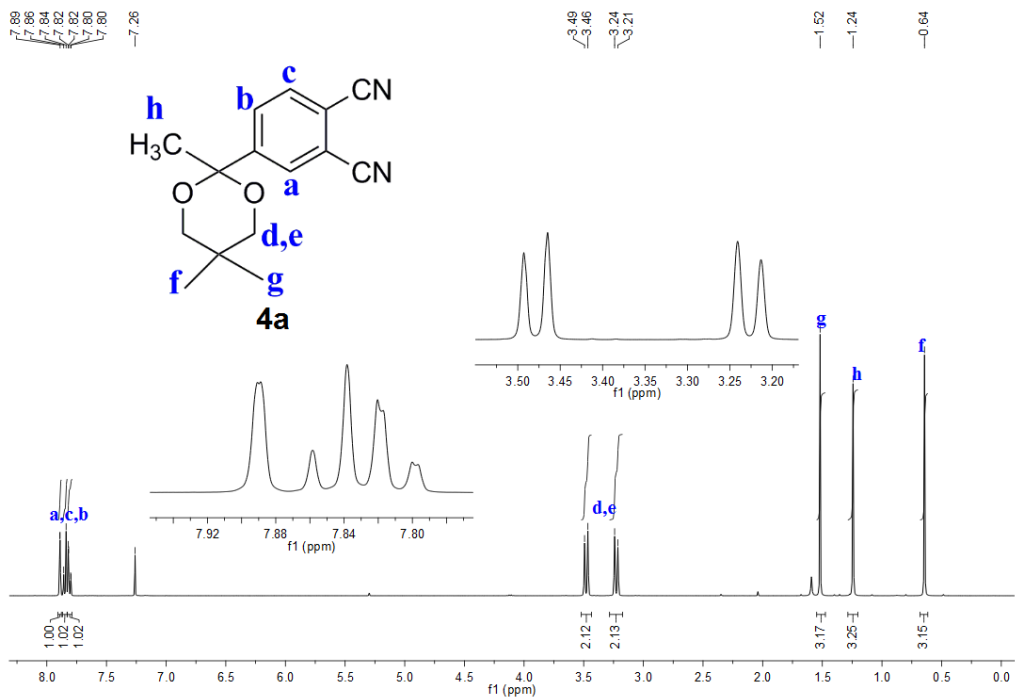
		m/z	error(mDa)	error(ppm)
Calculated value		1528.9970	-	-
Experiment value	1	1528.9943	- 2.7	- 1.8
	2	1528.9957	- 1.3	- 0.9
	3	1528.9950	- 2.0	- 1.3

These experimental determined values are associated with an ion of elementary composition $C_9H_{136}N_8O_4Zn^{+\bullet}$.

Mass spectrum measurements by MALDI putting into evidence the molecular ion $M^{+\bullet}$ from the sample.



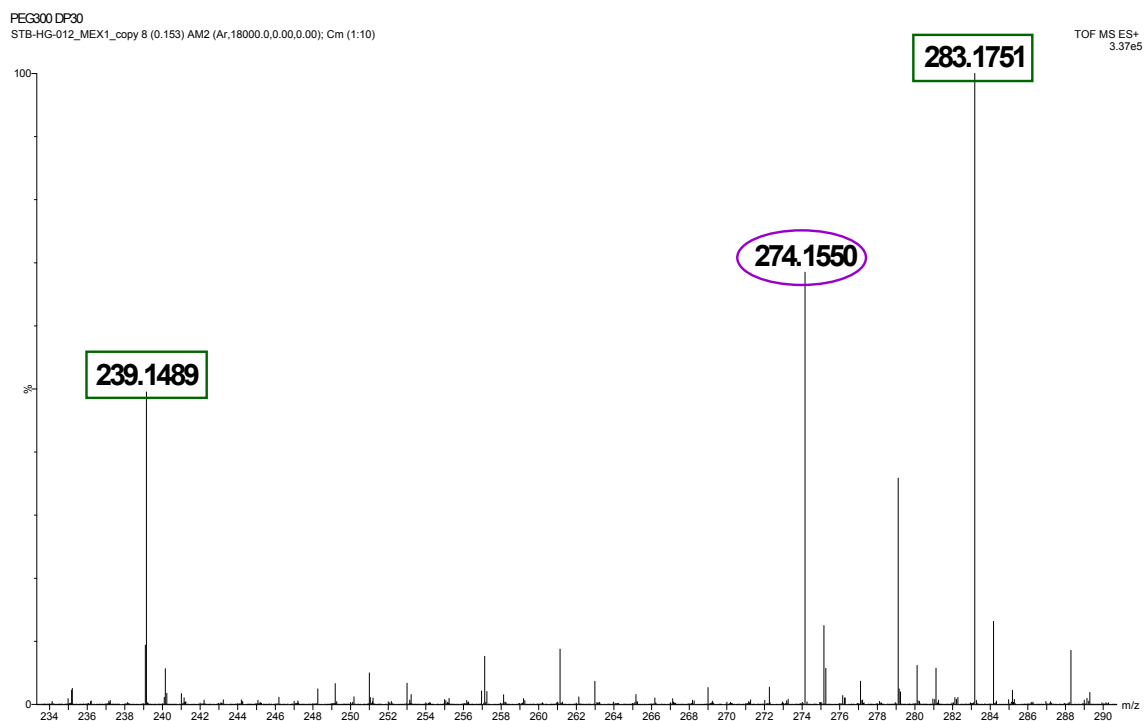
High Resolution Mass Spectrum in the ion molecular $M^{+\bullet}$ mode of MALDI of the sample **ZnPc-6d**. The targeted ion is detected at m/z 1528.9957 (violet ellipse) while the peaks retained for internal calibration are observed at m/z 1517.7139 and m/z 1579.6614 (green rectangles).



		m/z	error (mDa)	error (ppm)
Calculated value		274.1550	-	-
Experiment value	1	274.1550	0	0
	2	274.1551	+ 0.1	+ 0.4
	3	274.1550	0	0

These experimental determined values are associated with an ion of elementary composition $C_{15}H_{20}N_3O_2^+$.

HR-MS measurements by electrospray ionization in positive mode putting into evidence the ion $[M+NH_4]^+$ from the sample.

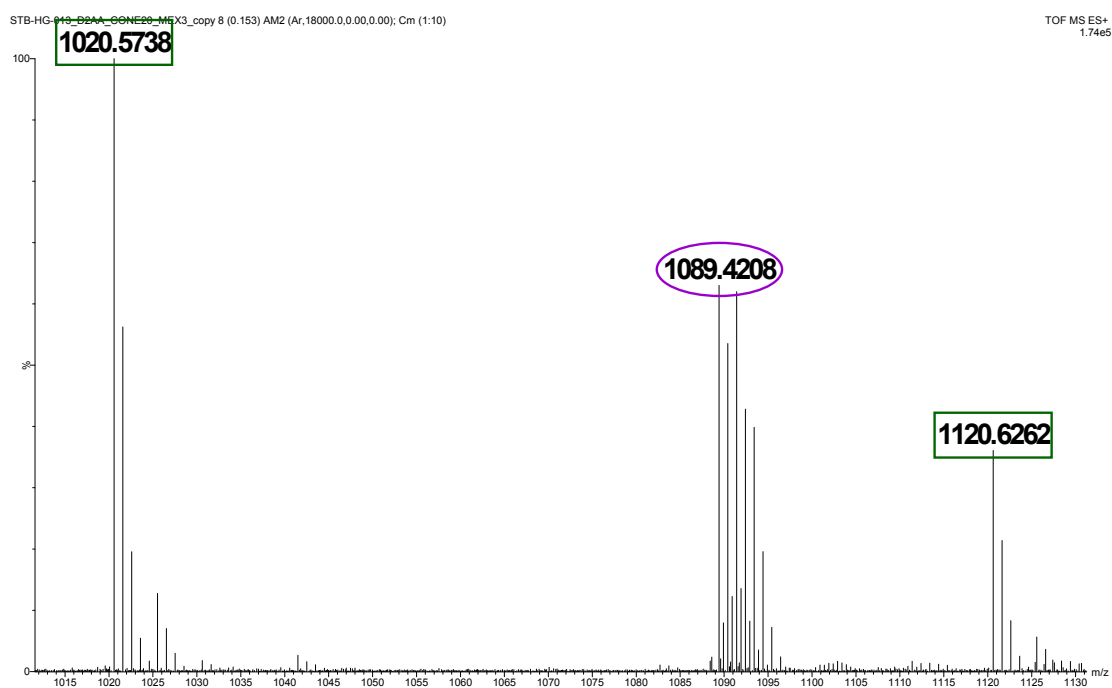


High Resolution Mass Spectrum in the positive mode of electrospray ionization of the sample **4a**. The targeted ion is detected at m/z 274.1550 (violet ellipse) while the peaks retained for internal calibration are observed at m/z 239.1489 and m/z 283.1751 (green rectangles).

		m/z	error (mDa)	error (ppm)
Calculated value		1089.4211	-	-
Experiment values	1	1089.4215	+ 0.4	+ 0.4
	2	1089.4216	+ 0.5	+ 0.5
	3	1089.4208	- 0.3	- 0.3

These experimental determined values are associated with an ion of elementary composition $C_{60}H_{65}N_8O_8Zn^+$.

HR-MS measurements by electrospray ionization putting into evidence the ion $[M+H]^+$ in positive mode from the sample.

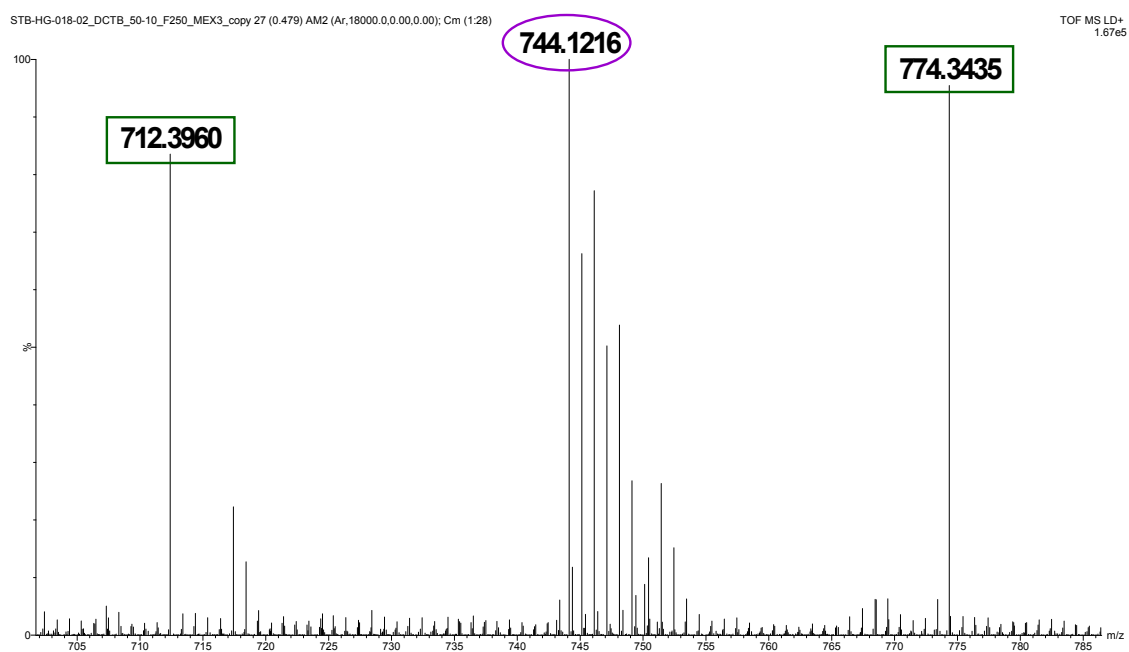


High Resolution Mass Spectrum in the positive mode of electrospray ionization of the sample **ZnPc-5a**. The targeted ion is detected at m/z 1089.4208 (violet ellipse) while the peaks retained for internal calibration are observed at m/z 1020.5738 and m/z 1120.6262 (green rectangles).

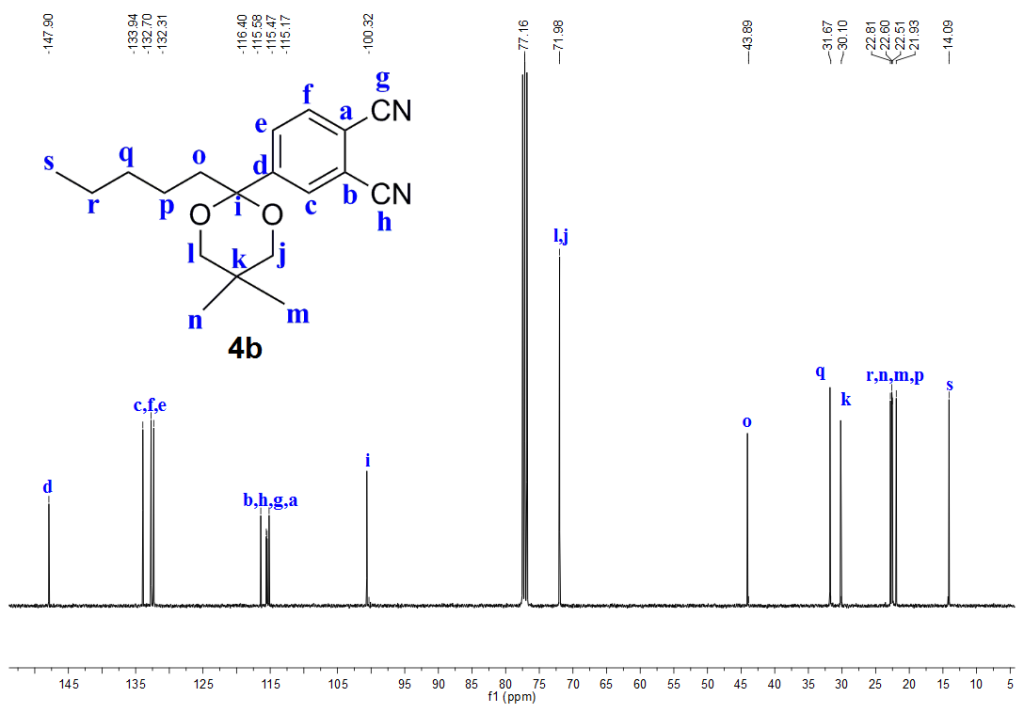
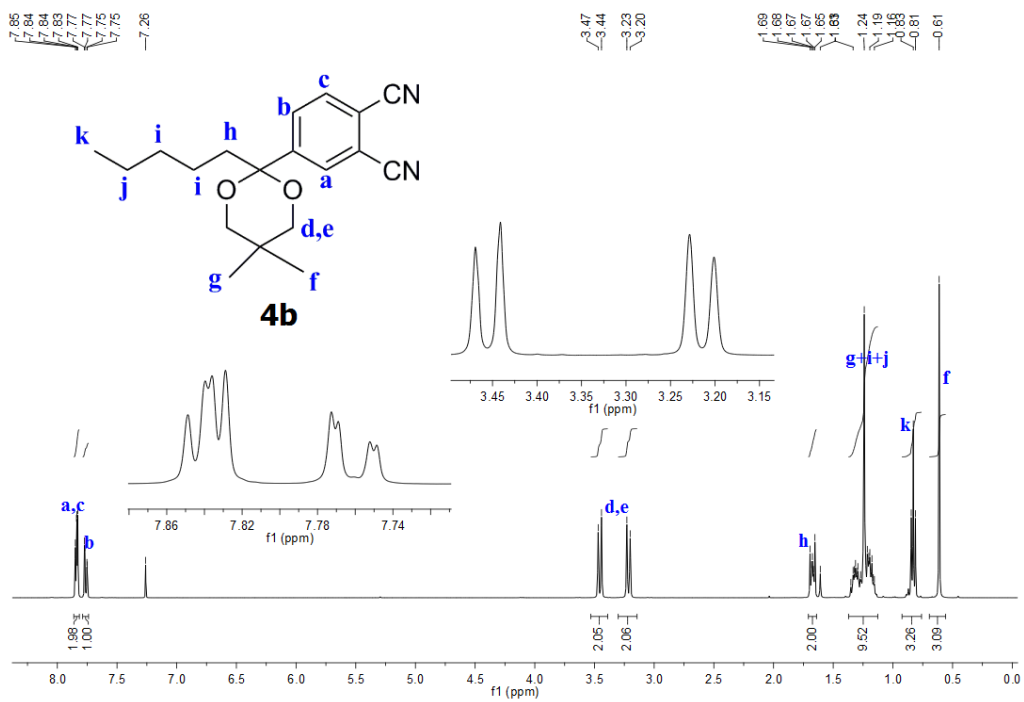
		m/z	error (mDa)	error (ppm)
Calculated value		744.1206	-	-
Experiment value	1	744.1222	+ 1.6	+ 2.2
	2	744.1223	+ 1.7	+ 2.3
	3	744.1216	+ 1.0	+ 1.3

These experimental determined values are associated with an ion of elementary composition $C_{40}H_{24}N_8O_4Zn^{+\bullet}$.

Mass spectrum measurements by electrospray ionization putting into evidence the ion $M^{+\bullet}$ from the sample.



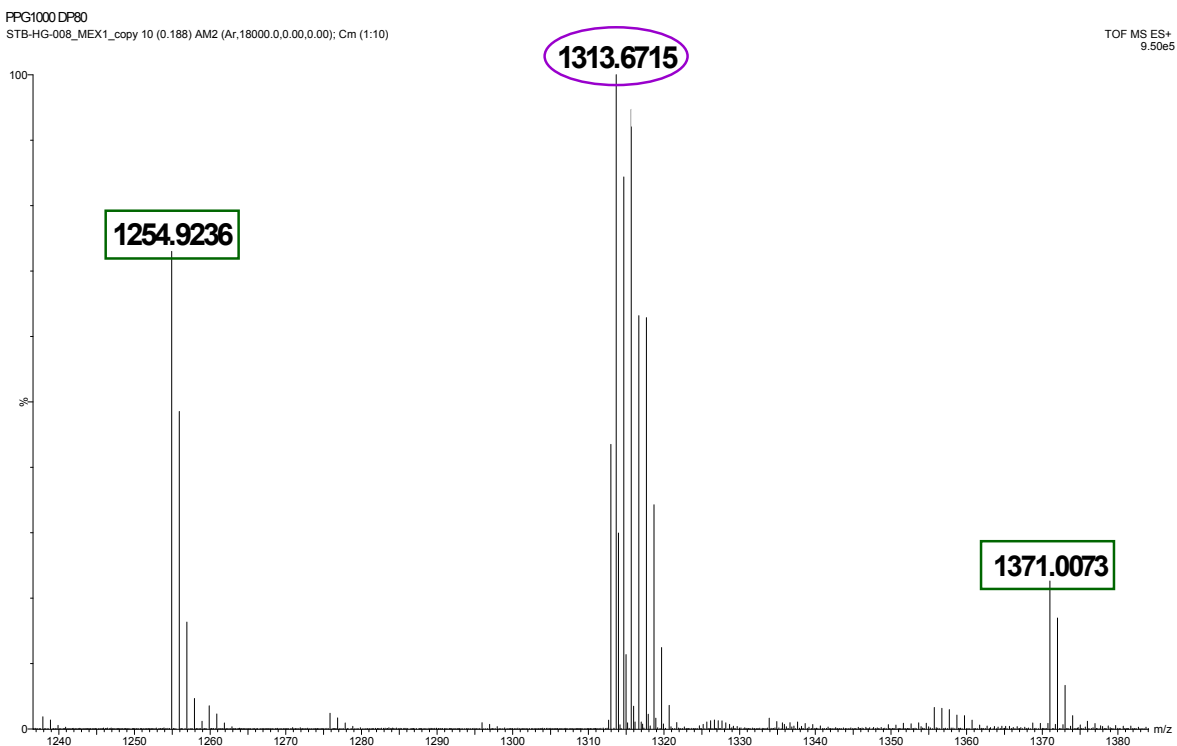
High Resolution Mass Spectrum in the ion $M^{+\bullet}$ mode of electrospray ionization of the sample **ZnPc-6a**. The targeted ion is detected at m/z 744.1216 (magenta ellipse) while the peaks retained for internal calibration are observed at m/z 712.3960 and m/z 744.3435 (green rectangles).



		m/z	error (mDa)	error (ppm)
Calculated value		1313.6715	-	-
Experiment values	1	1313.6715	0	0
	2	1313.6715	0	0
	3	1313.6714	- 0.1	- 0.1

These experimental determined values are associated with an ion of elementary composition $C_{76}H_{97}N_8O_8Zn^+$.

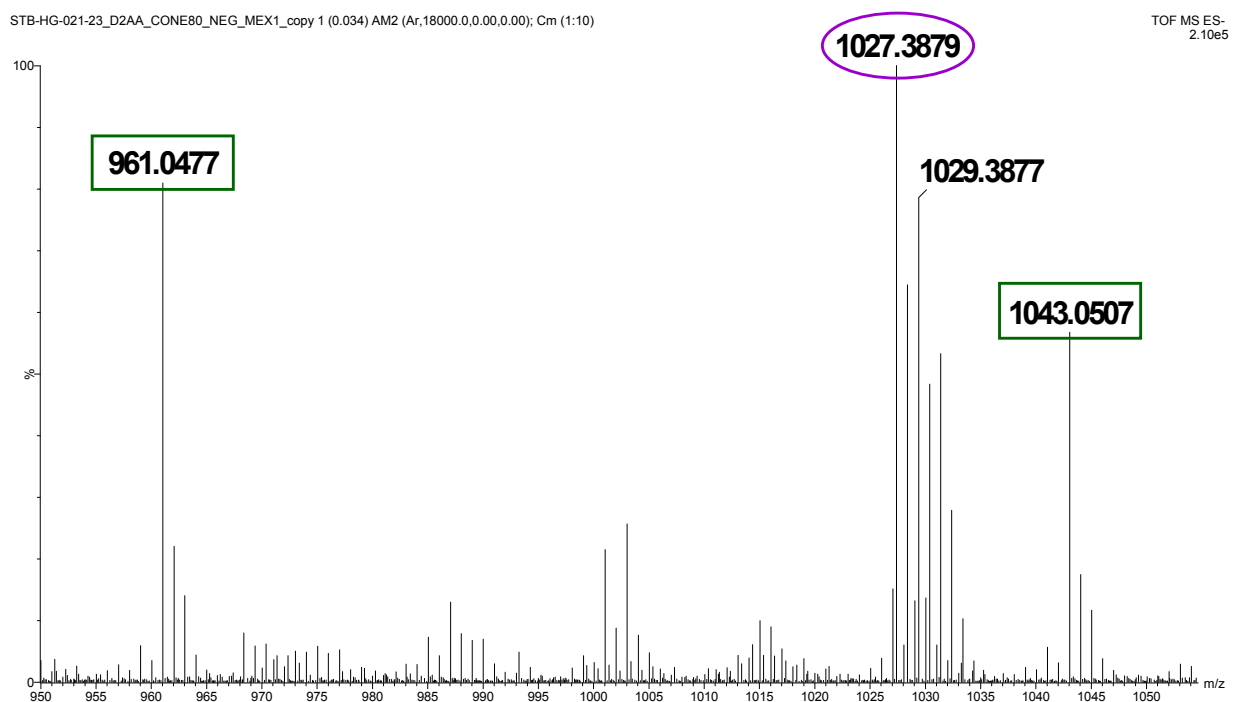
HR-MS measurements by electrospray ionization putting into evidence the ion $[M+H]^+$ in positive mode from the sample.



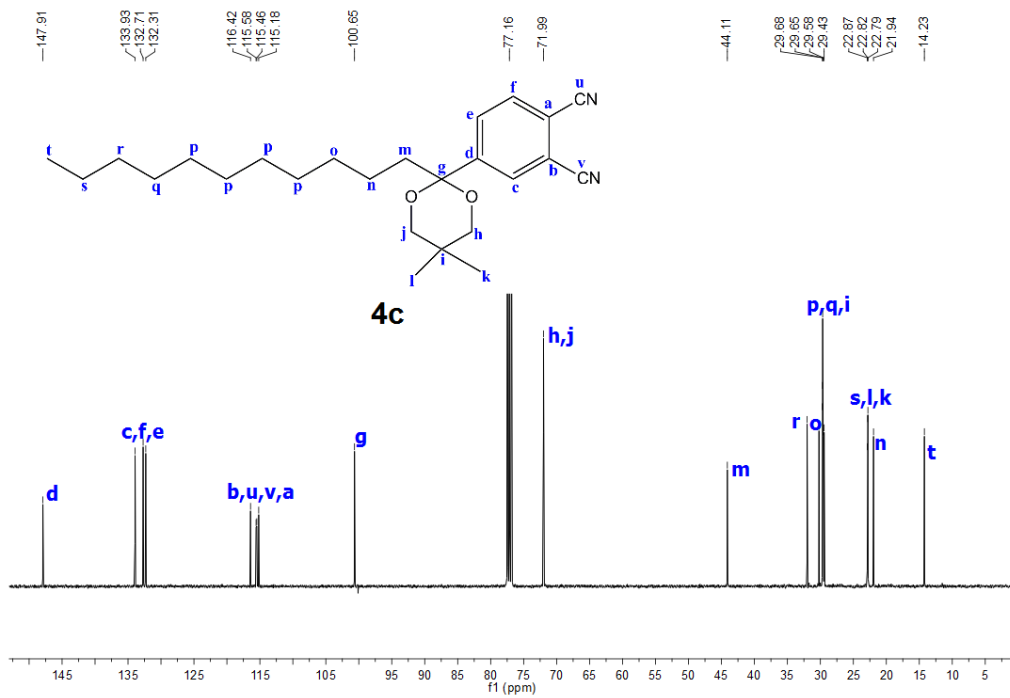
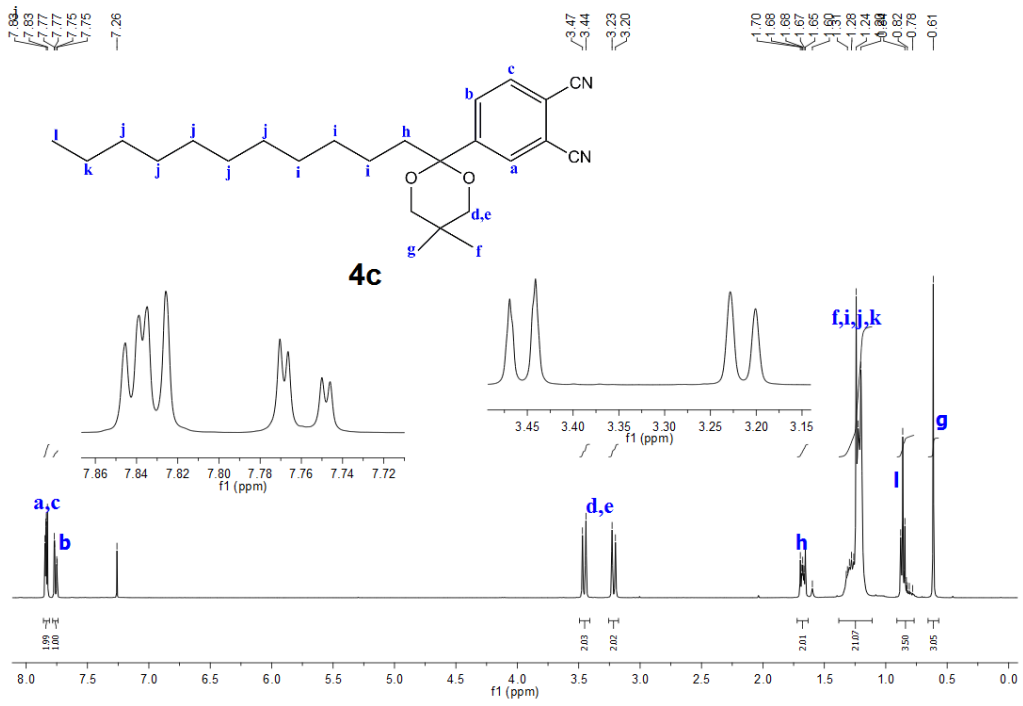
High Resolution Mass Spectrum in the positive mode of electrospray ionization of the sample **ZnPc-5b**. The targeted ion is detected at m/z 1313.6715 (violet ellipse) while the peaks retained for internal calibration are observed at m/z 1254.9236 and m/z 1371.0073 (green rectangles).

		m/z	error (mDa)	error (ppm)
Calculated value		1027.3855	-	-
Experiment value	1	1027.3879	+ 2.4	+ 2.3
	2	1027.3882	+ 2.7	+ 2.6
	3	1027.3879	+ 2.4	+ 2.3
These experimental determined values are associated with an ion of elementary composition $C_{58}H_{59}N_8O_6Zn^-$.				

Mass spectrum measurements by ESI into evidence the negative ion $[M+CH_3COO]^-$ mode from the sample.

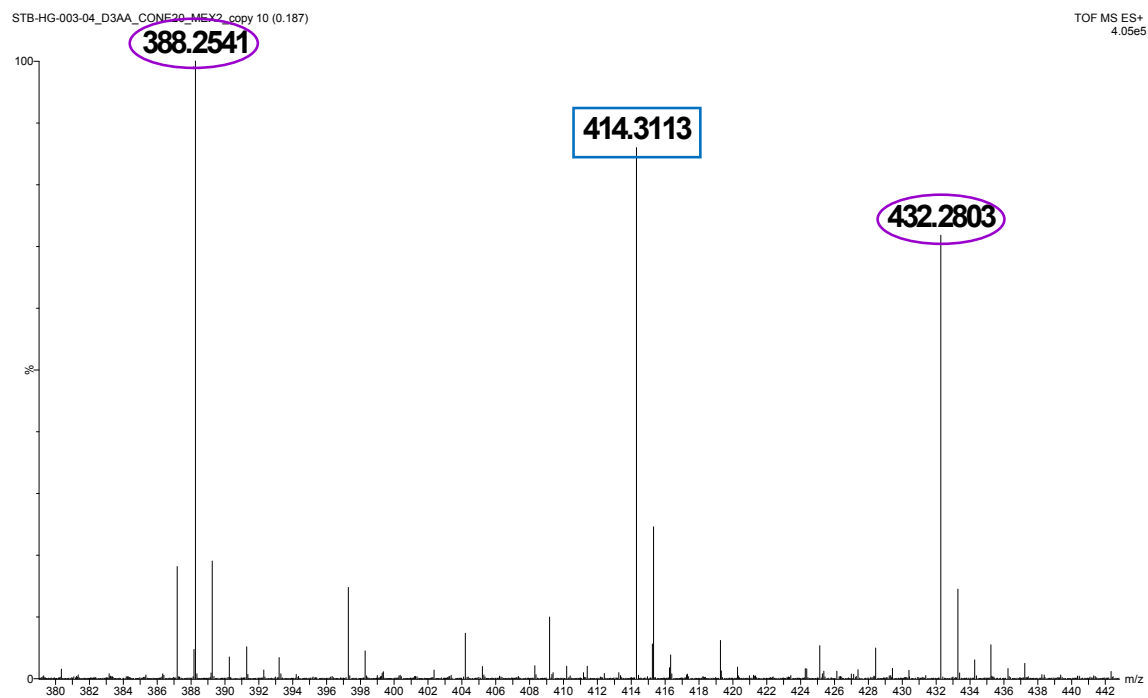


High Resolution Mass Spectrum in the negative ion $[M+CH_3COO]^-$ mode of ESI of the sample **ZnPc-6b**. The targeted ion is detected at m/z 1027.3879 (violet ellipse) while the peaks retained for internal calibration are observed at m/z 961.0477 and m/z 1043.0507 (green rectangles).



		m/z	error (mDa)	error (ppm)
Calculated value		414.3115	-	-
Experiment value	1	414.3110	- 0.5	- 1.2
	2	414.3113	- 0.2	- 0.5
	3	414.3111	- 0.4	- 1.0
These experimental determined values are associated with an ion of elementary composition $C_{25}H_{40}N_3O_2^+$.				

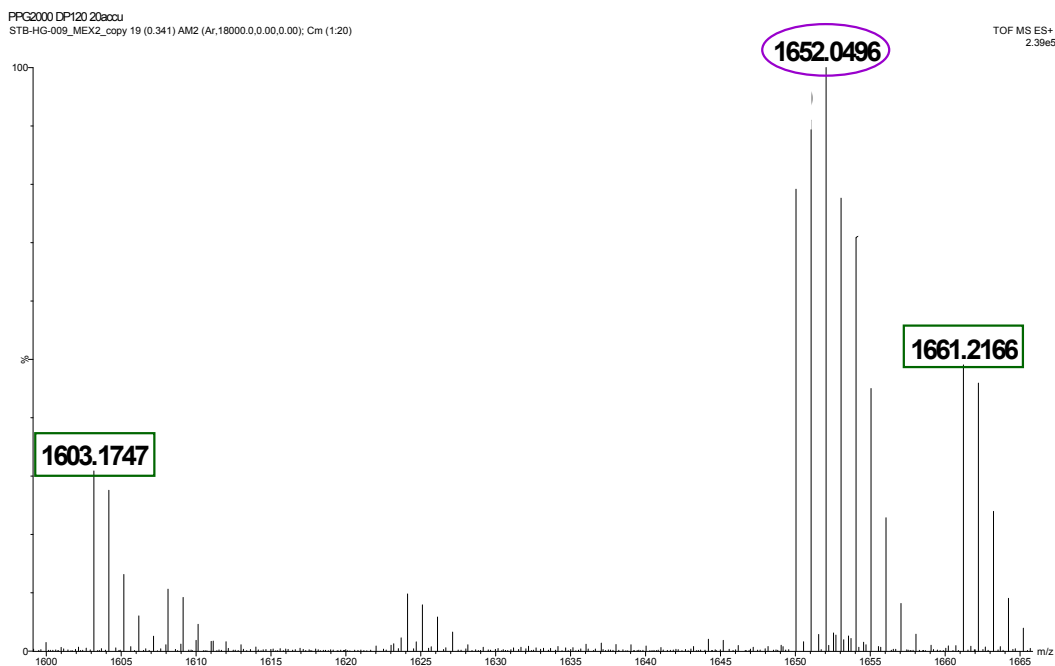
ESI-HR-MS measurements by electrospray ionization in positive mode putting into evidence the ion $[M+NH_4]^+$ from the sample.



High Resolution Mass Spectrum in the positive mode of electrospray ionization of the sample **4c**. The targeted ion is detected at m/z 414.3113 (blue rectangle) while the peaks retained for internal calibration are observed at m/z 388.2541 and m/z 432.2803 (violet ellipses).

		m/z	error (mDa)	error (ppm)
Calculated value		1652.0492	-	-
Experiment values	1	1652.0499	+ 0.7	+ 0.4
	2	1652.0496	+ 0.4	+ 0.2
	3	1652.0496	+ 0.4	+ 0.2

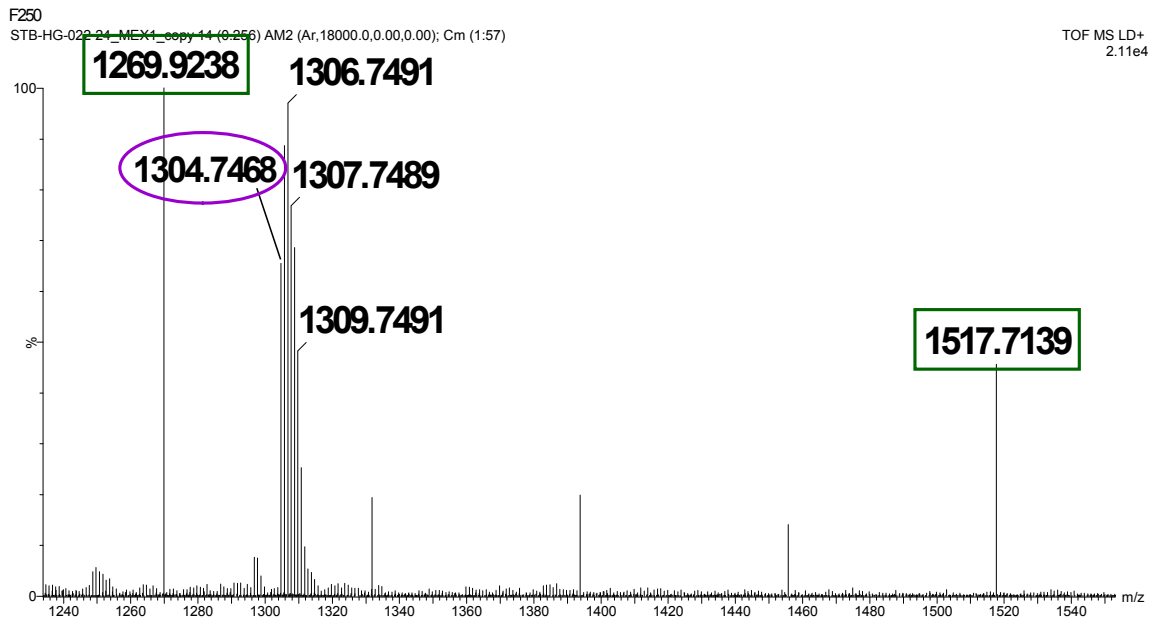
These experimental determined values are associated with an ion of elementary composition $C_{100}H_{145}N_8O_8Zn^+$. HR-MS measurements by electrospray ionization in positive mode putting into evidence the ion $[M+H]^+$.



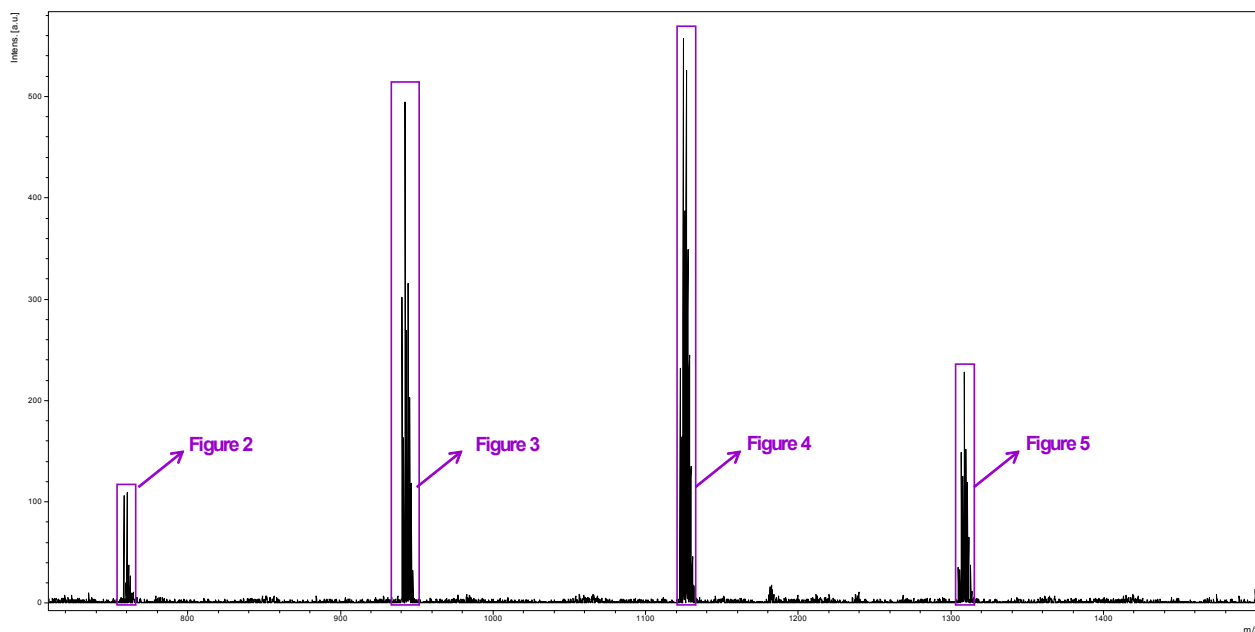
High Resolution Mass Spectrum in the positive mode of electrospray ionization of the sample **ZnPc-5c**. The targeted ion is detected at m/z 1652.0496 (violet ellipse) while the peaks retained for internal calibration are observed at m/z 1603.1747 and m/z 1661.2166 (green rectangles).

		m/z	error (mDa)	error (ppm)
Calculated value		1304.7467	-	-
Experimental values	1	1304.7468	+ 0.1	+ 0.1
	2	1304.7483	+ 1.6	+ 1.2
	3	1304.7465	- 0.2	- 0.2

These experimental determined values are associated with an M⁺ ion of elementary composition C₈₀H₁₀₄N₈O₄Zn⁺.



High Resolution Mass Spectrum in the positive ion molecular mode of MALDI of the sample **ZnPc-6c**. The targeted ion M⁺ is detected at m/z 1304.7468 (magenta ellipse) while the peaks retained for internal calibration are observed at m/z 1269.9238 and m/z 1517.7139 (green rectangles).



Negative ion MALDI-TOF mass spectrum of a sample obtained by the direct condensation of a 3-lauroylphthalodinitrile with the unsubstituted phthalodinitrile. The individual peaks corresponding to the AB_3 , A_2B_2 , A_3B and A_4 (as denoted in Scheme 2 of the main text) are presented together with the calculated isotopic patterns in the next four figures.

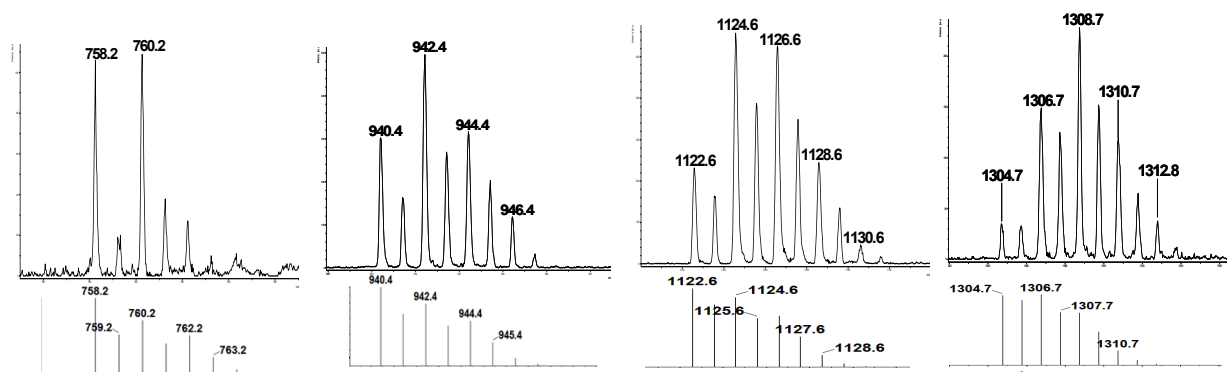
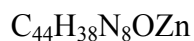


Fig. 3: A_2B_2



Calcd.: 758.2 Da

Fig. 4: A_3B



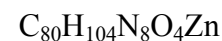
Calcd.: 940.4 Da

Fig. 5: A_4



Calcd.: 1122.6 Da

Fig. 2: AB_3



Calcd.: 1304.7 Da