Supporting Information

Supramolecular Liquid Crystalline Dendrimers with a Porphyrin core and Functional Carboxylic Acid Dendrons

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Materials and Methods

Reagents were purchased from Aldrich and were used as received. Anhydrous THF was purchased from Scharlau and dried using a solvent purification system. 5,10,15,20-Tetra(4-pyridyl)porphyrin (**TPyP**) and Zn(II) 5,10,15,20-tetra(4-pyridyl)porphyrin (**ZnTPyP**) were purchased from Frontier Scientific.

The infrared spectra of all the compounds were obtained with a Nicolet Avatar 360 FTIR spectrophotometer in the 400–4000 cm^{-1} spectral range using KBr pellets and NaCl cells. NMR data were obtained on Bruker AVANCE spectrometers operating at 500, 400 and 300 MHz for ^{1}H and 125, 100 and 75 MHz for ^{13}C. Elemental analyses were performed using a Perkin-Elmer 240C microanalyzer. Mass Spectrometry was performed using a MALDI+/TOF Brüker Microflex system with a DIT + NaFTA matrix and MicroTOF Brüker system for exact mass measurements.

Mesogenic behaviour and transition temperatures were determined using an Olympus DP12 polarizing optical microscope equipped with a Linkam TMS91 hot stage and a CS196 central processor. Differential scanning calorimetry (DSC) experiments were performed on DSC TA Instruments Q-20 and Q-2000 systems. Samples were sealed in aluminium pans and a scanning rate of 10 °C•min^{-1} under a nitrogen atmosphere was used. The systems were calibrated with indium (156.6 °C; 28.4 J•g^{-1}) as the standard. Three thermal cycles were carried out. The mesophase transition temperatures were read at the maximum of the corresponding peaks. Thermogravimetric analysis (TGA) was performed on a TA instruments TGA Q5000 at a rate of 10 ºC•min^{-1} under an argon atmosphere.

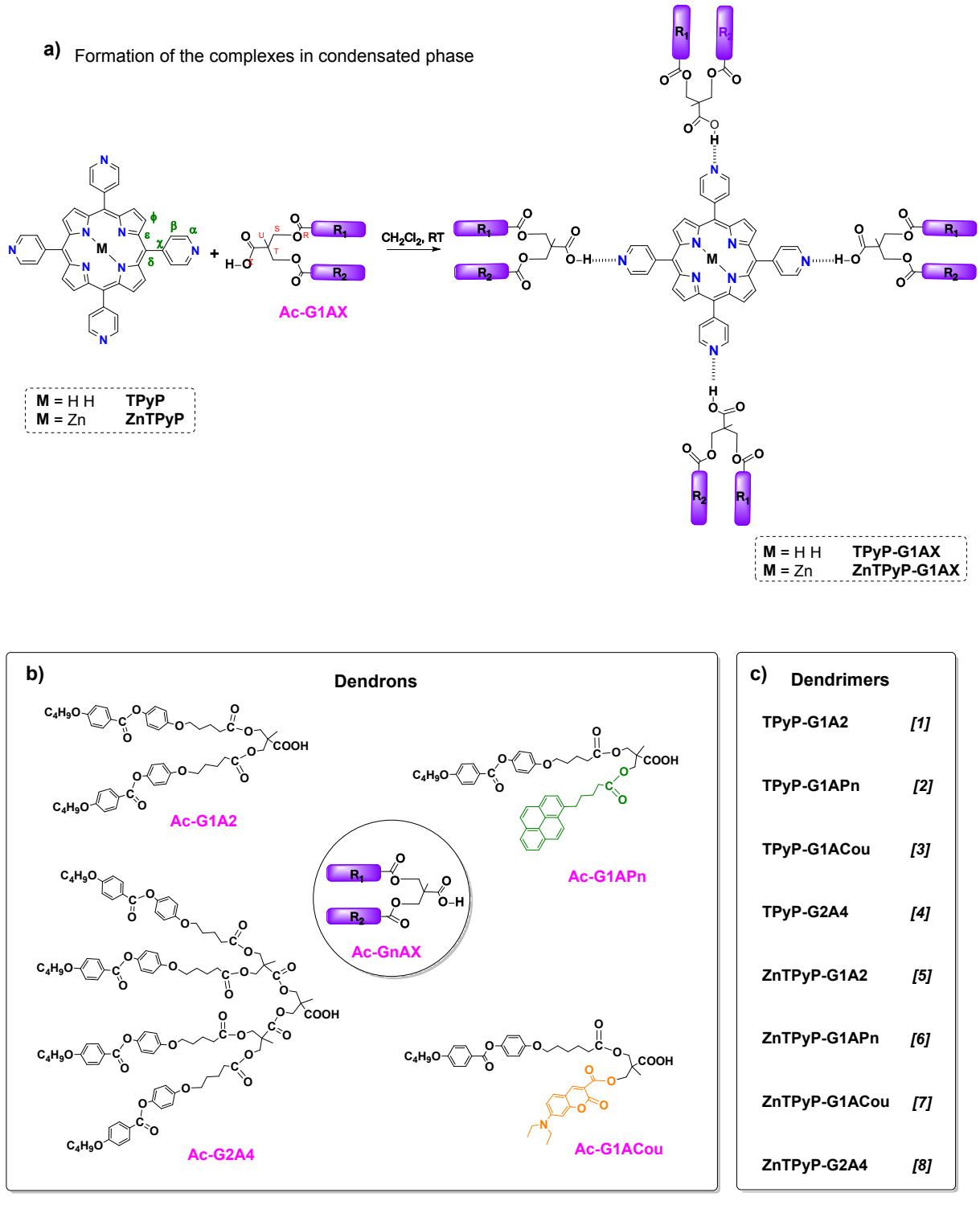
XRD experiments were performed on a pinhole camera (Anton-Paar) operating with a point-focused Ni-filtered Cu-Kα beam. Lindemann glass capillaries with 0.9 mm diameter were used to contain the sample and, where necessary, a variable-temperature attachment was used to heat the sample. The patterns were collected on flat photographic film perpendicular to the X-ray beam. Bragg's law was used to obtain the spacing.

UV-vis absorption spectra were measured with a UV4-200 from ATI-Unicam using 10^{-5}–10^{-6} M solutions in CH_2Cl_2 (HPLC Grade). Fluorescence spectra were measured with a Perkin Elmer LS50B fluorescence spectrometer using solutions in CH_2Cl_2 of ca. 0.01 absorbance (about 10^{-8}–10^{-9} M) under excitation at the absorption maximum

1. Synthetic procedures and chemical compound information

Synthesis and characterization of the compounds

The synthetic route followed for the preparation of dendrimers is shown in Scheme S1



Scheme S1. Schematic representation of: **a)** Synthetic route and atom labels for first generation of dendrimer complexes **TPyP-G1AX** or **ZnTPyP-G1AX**, **b)** carboxylic acid dendrons of the first (**Ac-G1AX**) and second generation (**Ac-G2A4**), **c)** nomenclature of supramolecular dendrimers.

Synthesis of the dendrons

The synthetic route followed for the preparation of symmetric carboxylic acid dendrons is described by us in *Chem. Eur. J. 2014, 20, 10027 – 10037.*

General procedure to prepare the hydrogen-bonded dendrimers

To a solution of porphyrin (**TPyP** or **ZnTPyP**) in the minimum volume of dry CH_2Cl_2 was added a solution of the appropriate carboxylic acid dendron in dry CH_2Cl_2, in a 1:4 ratio. Solvent was slowly removing under mechanical stirring at room temperature. The samples of the complexes were heated above the clearing temperature and subsequent cooling yielded homogenous materials in all cases.

Dendrimer TPyP-G1A2 [1]:

Anal. calcd. for $C_{236}H_{258}N_8O_{56}$: C, 69.09%; H, 6.34%; N, 2.73%. Found: C, 69.21%; H, 6.43%; N, 2.53%.

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 25ºC, TMS) δ 9.10-9.03 (m, 8H), 8.85 (s, 8H), 8.26-8.19 (m, 8H), 8.08-8.00 (m, 16H), 7.10-7.03 (m, 16H), 7.00- 6.77 (m, 32H), 4.32 (ABq, 16H), 4.11-3.85 (m, 32H), 2.45 (m, 16H), 1.93-1.64 (m, 48H), 1.48 (m, 16H), 1.35-1.29 (m, 12H), 0.98 (t, *J* = 7.4 Hz, 24H), -2.99 (s, 2H). The shift of -COO***H*** it is a low intensity broad peak and overlap to other signals. **^{13}C NMR** (125 MHz, $C_2D_2Cl_4$, 25ºC, TMS) δ 175.80, 172.84, 165.13, 163.24, 156.29, 150.59, 146.92, 144.05, 131.38, 131.93, 129.53, 122.44, 121.09, 117.31, 114.90, 114.14, 67.85, 67.65, 65.22, 45.79, 33.55, 30.86, 28.38, 21.39, 19.00, 17.79, 13.74.

IR (KBr) (cm^{-1}): 3442 (O–H), 3312 (N–H), 2400-2600 (O–H asoc), 1733 (C=O). **UV–Vis** (CH_2Cl_2, 10^{-5} mol L^{-1}) λ/nm: 416, 456, 515, 549, 589, 645.

Dendrimer TPyP-G1APn [2]:

Anal. calcd. for $C_{228}H_{218}N_8O_{40}$: C, 73.81%; H, 5.92%; N, 3.02%. Found: C, 72.99%; H, 6.40%; N, 2.71%

^{1}H NMR (500 MHz, $CDCl_3$, 25ºC, TMS) δ 9.12-8.93 (m, 8H), 8.68 (s, 8H), 8.25 (d, *J* = 9.2 Hz, 4H), 8.17-7.72 (m, 48H), 7.08-6.96 (m, 8H), 6.91-6.75 (m, 16H), 4.53-4.18 (m, 16H), 3.97 (t, *J* = 6.5 Hz, 8H), 3.94-3.76 (m, 8H), 3.34 (t, *J* = 7.8 Hz, 8H), 2.56-2.31 (m, 16H), 2.24-2.10 (m, 8H), 1.94-1.64 (m, 24H), 1.54-1.39 (m, 8H), 1.35-1.29 (m, 12H), 0.98 (t, *J* = 7.4 Hz, 12H), -2.94 (s, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25ºC, TMS) δ 176.98, 173.13, 173.05, 165.24, 163.38, 156.49, 150.77, 147.18, 144.45, 135.61, 132.10, 131.30, 130.82, 129.91, 129.58, 128.66, 127.39, 127.32, 126.61, 125.74, 125.03, 124.90, 124.80, 124.70, 123.24, 122.45, 121.58, 117.42, 115.02, 114.16, 67.94, 67.70, 65.73, 46.25, 33.77, 32.66, 31.11, 28.59, 21.57, 19.17, 18.14, 13.80.

IR (KBr) (cm^{-1}): 3450 (O–H), 3312 (N–H), 2400-2600 (O–H asoc), 1730 (C=O). **UV–Vis** (CH_2Cl_2, 10^{-5} mol L^{-1}) λ/nm: 266, 277, 314, 328, 344, 416, 512, 547, 587, 642.

Dendrimer TPyP-G1ACou [3]:

Anal. calcd. for $C_{204}H_{214}N_{12}O_{48}$: C, 68.02%; H, 5.99%; N, 4.67%; found: C, 68.75%; H, 6.53%; N, 5.28%.

^{1}H NMR (500 MHz, $CDCl_3$, 25ºC, TMS) δ 9.13-9.04 (m, 8H), 8.85 (s, 8H), 8.40 (s, 4H), 8.24-8.17 (m, 8H), 8.05-7.97 (m, 8H), 7.35 (d, *J* = 9.0 Hz, 4H), 7.07-7.00 (m, 8H), 6.95-6.80 (m, 16H), 6.59 (dd, *J* = 8.9, 2.4 Hz, 4H), 6.41 (d, *J* = 2.4 Hz, 4H), 4.63-4.36 (2ABq ,16H), 4.16-3.92 (m, 16H), 3.43 (q, *J* = 7.1 Hz, 16H), 2.53-2.39 (m, 8H), 1.89-1.72 (m, 24H), 1.57-1.36 (m, 20H), 1.22 (t, *J* = 7.4 Hz, 24H), 0.98 (t, *J* = 7.4 Hz, 12H), -2.95 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$, 25ºC, TMS) δ 176.38, 173.04, 165.23, 163.62, 163.36, 158.53, 158.24, 156.55, 153.08, 150.72,

149.36, 147.38, 144.41, 132.10, 131.8 (hsqc), 131.29, 129.62, 125.51, 122.46, 121.55, 117.58, 115.04, 114.14, 109.65, 108.01, 107.66, 96.64, 67.94, 67.78, 66.03, 65.77, 46.36, 45.10, 33.83, 31.12, 30.32, 28.64, 21.62, 19.18, 18.18, 13.82, 12.44.

IR (KBr) (cm^{-1}): 3312 (N–H), 2600-2700 (O–H), 1732 (C=O). **UV–Vis** (CH_2Cl_2, 10^{-5} mol L^{-1}) λ/nm: 262, 420, 515, 550, 590, 646

Dendrimer TPyP-G2A4 [4]:

Anal. calcd. for $C_{452}H_{514}N_8O_{120}$: C, 68.04%; H, 6.49%; N, 1.40%. Found: C, 67.27%; H, 7.27%; N, 0.74%

^{1}H NMR (500 MHz, $CDCl_3$, 25ºC, TMS) δ 9.11-9.02 (m, 8H), 8.85 (s, 8H), 8.26-8.15 (m, 8H), 8.12-8.00 (m, 32H), 7.06-6.97 (m, 32H), 6.97-6.77 (m, 64H), 4.53- 4.11 (m, 44H), 3.99 (t, *J* = 5.0 Hz, 32H), 4.10-3.83 (m, 32H), 3.74-3.65 (m, 4H), 2.49-3.36 (m, 32H), 1.94-1.64 (m, 96H), 1.56-1.44 (m, 32H), 1.41-1.17 (m, 36H), 0.98 (t, *J* = 7.4 Hz, 48H), -2.94 (s, 2H). The shift of -COO***H*** it is a low intensity broad peak and overlap to other signals. **^{13}C NMR** (125 MHz, $CDCl_3$, 25ºC, TMS) δ 175.42, 174.68, 173.55, 173.40, 172.92, 172.86, 172.38, 172.18, 165.30, 163.41, 156.49, 150.91, 147.14, 144.43, 132.37, 132.16, 129.71, 122.48, 121.54, 117.53, 115.00, 114.41, 114.19, 67.93, 67.71, 65.92, 65.71, 65.62, 65.30, 48.67, 46.54, 46.46, 46.40, 46.31, 33.65, 31.11, 28.62, 21.55, 19.17, 17.86, 17.43, 13.82. (The ^{13}C signals of dendron focal point (COO, C_q, CH_3) appear unfolded).

IR (KBr) (cm^{-1}): 3312 (N–H), 2400-2600 (O–H asoc), 1733 (C=O). **UV–Vis** (CH_2Cl_2, 10^{-5} mol L^{-1}) λ/nm: 416, 456, 515, 549,589, 645.

Dendrimer ZnTPyP-G1A2 [5]:

Anal. calcd. for $C_{236}H_{256}N_8O_{56}Zn$: C, 68.04%; H, 6.19%; N, 2.69%. Found: C, 63.07%; H, 6.28%; N, 2.35%.

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 25ºC, TMS) δ 9.4-8.3 (br, 24H), 8.10-8.00 (m, 16H), 7.10-7.02 (m, 16H), 6.97-6.87 (m, 32H), 4.40-4.25 (ABq, 16H), 4.01-3.85 (m, 32H), 2.05-2.38 (m, 16H), 1.86-1.78 (m, 32H), 1.53-1.42 (m, 16H), 1.39-1.29 (m, 12H), 1.26 (d, *J* = 14.4 Hz, 12H), 0.97 (t, *J* = 7.4 Hz, 24H).

^{13}C NMR (101 MHz, $C_2D_2Cl_4$, 25ºC, TMS) δ 175.75, 172.88, 165.14, 163.24, 156.28, 151.32, 148.74, 146.60, 144.04, 131.93, 131.62, 129.18, 122.43, 121.08, 120.09, 114.89, 114.18, 114.14, 74.37, 73.97, 73.82, 73.78, 73.70, 73.50, 73.42, 67.85, 67.66, 65.28, 45.80, 33.56, 30.86, 28.39, 21.38, 19.00, 17.86, 13.74.

IR (KBr) (cm^{-1}): 3238 (O–H), 2400-2600 (O–H asoc), 1733 (C=O). **UV–Vis** (CH_2Cl_2, 10^{-5} mol L^{-1}) λ/nm: 262, 419, 450(sh), 577(sh)

Dendrimer ZnTPyP-G1APn [6]:

Anal. calcd. for $C_{228}H_{218}N_8O_{40}Zn$: C, 72.58%; H, 5.85%; N, 2.96%. Found: C, 71.12%; H, 7.03%; N, 2.23%

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 25ºC, TMS) δ 9.1-7.74 (m, 68H), 7.11-6.77 (m,24H), 4.48-4.19 (m, 16H), 4.01 (t, *J* = 6.5 Hz, 8H), 3.96-3.78 (m, 8H), 3.50-3.22 (m, 8H),), 2.63-2.29 (m, 16H), 2.26-2.06 (m, 8H), 1.94-1.64 (m, 24H), 1.58-1.39 (m, 8H), 1.38-1.11 (m, 12H), 0.98 (t, *J* = 7.4 Hz, 12H). **^{13}C NMR** (125 MHz, $C_2D_2Cl_4$, 25ºC, TMS) δ 172.97, 165.15, 163.26, 156.25, 151.42, 148.59, 146.54, 144.03, 135.54, 131.95, 130.98, 130.48, 129.88, 129.56, 128.33, 127.24, 126.49, 125.72, 124.74, 124.65, 123.07, 122.40, 121.12, 114.85, 114.16, 74.07, 73.96, 73.80, 73.70, 73.33, 67.85, 67.58, 65.43, 53.59, 45.93, 33.52, 32.40, 30.87, 28.34, 26.47, 22.55, 21.33, 19.01, 17.91, 14.07, 13.75.

IR (KBr) (cm^{-1}): 3199 (O–H), 2400-2600 (O–H asoc), 1733 (C=O). **UV–Vis** (CH_2Cl_2, 10^{-5} mol L^{-1}) λ/nm: 277, 328, 345, 419, 446, 570, 610.

Dendrimer ZnTPyP-G1ACou [7]:

Anal. calcd. for $C_{204}H_{212}N_{12}O_{48}Zn$: C, 66.85; H, 5.83%; N, 4.59%. Found: C, 65.89%; H, 6.62%; N, 4.15%.
^{1}H NMR (500 MHz, $CDCl_3$, 25ºC, TMS) δ 9.2-7.5 (br, 24H), 8.36 (s, 4H), 8.16-7.99 (m, 8H), 7.32 (d, *J* = 8.9 Hz, 4H), 7.12-6.82 (m, 24H), 6.58 (dd, *J* = 8.9, 2.4 Hz, 4H), 6.40 (d, *J* = 2.4 Hz, 4H), 4.56-4.29 (2ABq ,16H), 4.02 (t, *J* = 6.5 Hz, 8H), 3.98-3.90 (m, 8H), 3.42 (q, *J* = 7.1 Hz, 16H), 2.47-2.37 (m, 8H), 1.89-1.72 (m, 24H), 1.53-1.48 (m, 8H), 1.44-1.36 (m, 12H), 1.21 (t, *J* = 7.4 Hz, 24H), 0.98 (t, *J* = 7.4 Hz, 12H). **^{13}C NMR** (125 MHz, $CDCl_3$, 25ºC, TMS) δ 176.40, 172.95, 165.28, 163.60, 163.43, 158.56, 158.21, 156.57, 153.13, 151.68, 149.41, 148.95, 145.59, 144.49, 132.16, 131.72, 131.30, 129.59, 129.27, 122.46, 121.67, 115.40, 115.11, 114.22, 109.68, 108.02, 107.70, 96.68, 77.35, 77.27, 77.03, 76.96, 76.72, 76.64, 67.99, 67.83, 65.95, 65.68, 46.39, 45.11, 33.80, 31.15, 28.65, 21.62, 19.20, 18.10, 13.81, 12.45, 1.03.
IR (KBr) (cm^{-1}): 3206 (O–H), 2400-2600 (O–H asoc), 1734 (C=O). **UV–Vis** (CH_2Cl_2, 10^{-5} mol L^{-1}) λ/nm: 262, 314, 420, 561.

Dendrimer ZnTPyP-G2A4 [8]:

Anal. calcd. for $C_{452}H_{512}N_8O_{120}Zn$: C, 67.50%; H, 6.42%; N, 1.39%. Found: C, 66.50%; H, 6.34%; N, 1.28%.
^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 25ºC, TMS) δ 9.4-8.4 (br, 24H), 8.29-7.93 (m, 32H), 7.16-6.83 (m, 96H), 4.39-4.12 (m, 44H), 4.02 (t, *J* = 5.0 Hz, 32H), 3.99-3.87 (m, 32H), 3.85-3.5 (m, 4H), 2.49-4.31 (m, 32H), 1.94-1.76 (m, 96H), 1.56-1.40 (m, 32H), 1.41-1.17 (m, 36H), 0.97 (t, *J* = 7.5 Hz, 48H). **^{13}C NMR** (125 MHz, $C_2D_2Cl_4$, 130ºC, TMS) δ 172.08, 171.68, 164.65, 163.40, 156.45, 150.74, 149.10, 146.46, 144.92, 131.76, 131.73, 128.80, 122.08, 121.77, 115.43, 114.46, 68.27, 68.14, 65.90, 65.29, 46.67, 46.15, 33.44, 30.95, 28.54, 21.34, 18.81, 17.35, 17.19, 16.97, 13.17.
IR (KBr) (cm^{-1}): 3100-3040 (O-H), 2400-2600 (O–H asoc), 1735 (C=O). **UV–Vis** (CH_2Cl_2, 10^{-5} mol L^{-1}) λ/nm: 262, 337, 439, 573, 615.

2. Supporting Tables

Table S1. Photophysical data for dendrons and dendrimers

Compound	Absorbance λ_{abs} (nm)		Florescence λ_{em}(nm)
	Solution[a]	Film	Solution[b]
Ac-G1APn	266, 277, 314, 328, 344	266, 289, 300, 352, 369	377, 399
TPyP-G1APn	266, 277, 314, 328, 344, 416, 512, 547, 587, 642	266, 277, 314, 328, 344, 416, 512, 547, 587, 645	377, 398, 418
ZnTPyP-G1APn	277, 328, 345, 419, 446, 570, 610	*	377, 397, 418
Ac-G1ACou	262, 424	262, 417	458
TPyP-G1ACou	262, 420, 515, 550, 590, 646	262, 424, 516, 550, 592, 645	456
ZnTPyP-G1ACou	262, 314, 420, 561	*	456

[a]CH_2Cl_2 solution (10^{-5} mol L^{-1}). [b]CH_2Cl_2 solution (10^{-8} mol L^{-1}).

3. Supporting Figures

NMR Spectra

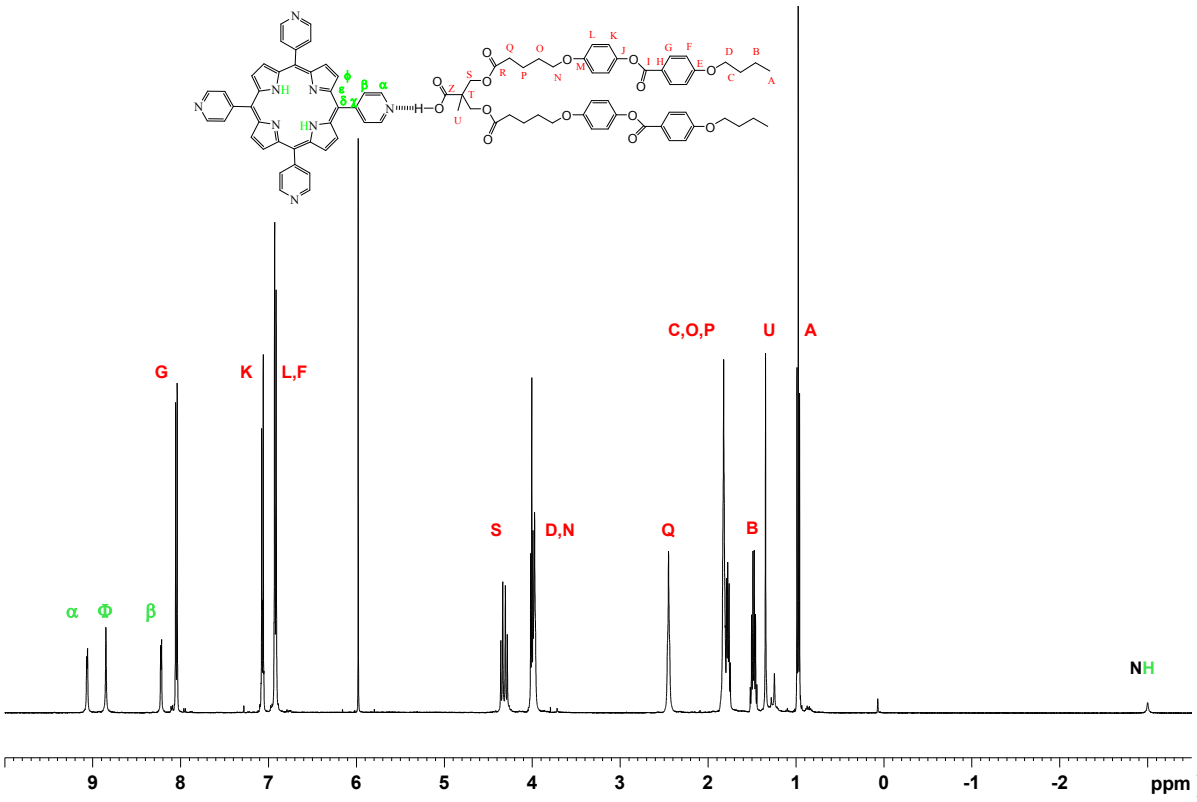


Figure S1. ^{1}H NMR spectrum of complex **TPyP-G1A2.** (500 MHz, $C_2D_2Cl_4$, 25ºC)

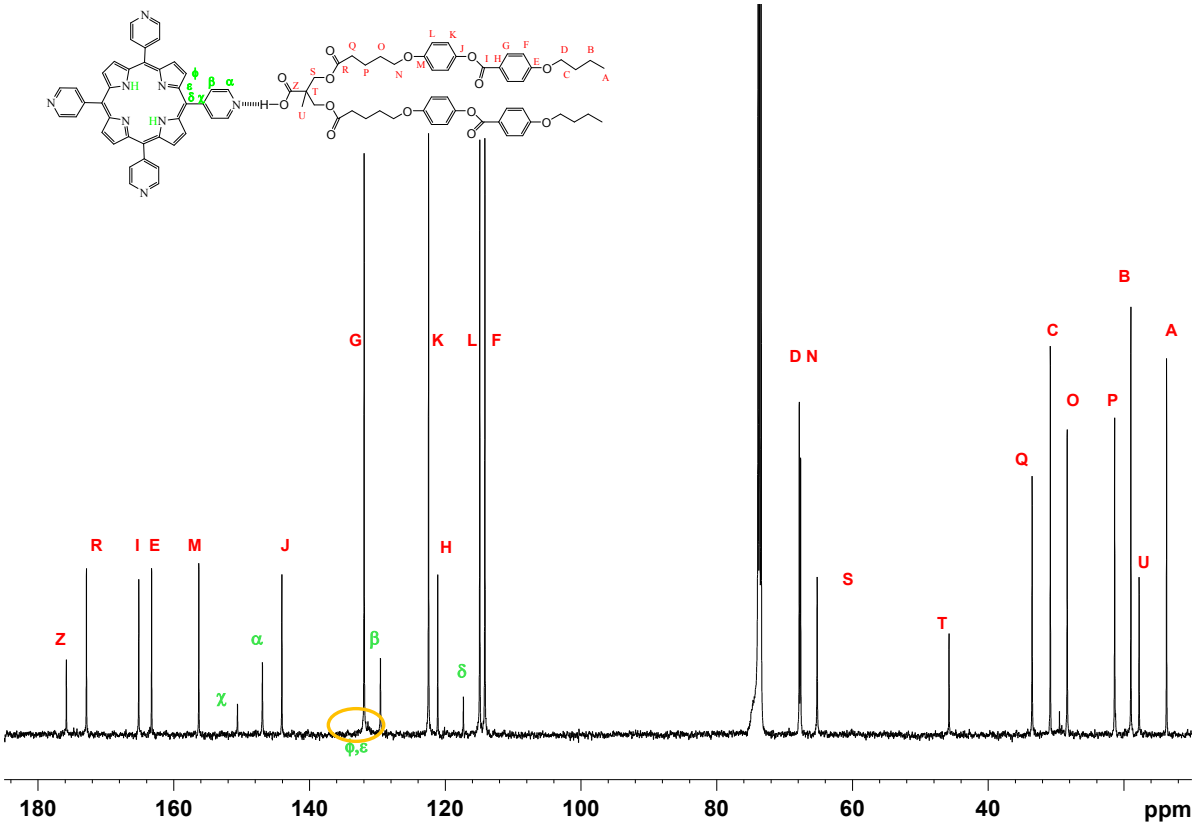


Figure S2. ^{13}C NMR spectrum of complex **TPyP-G1A2.** (500 MHz, $C_2D_2Cl_4$,25ºC)

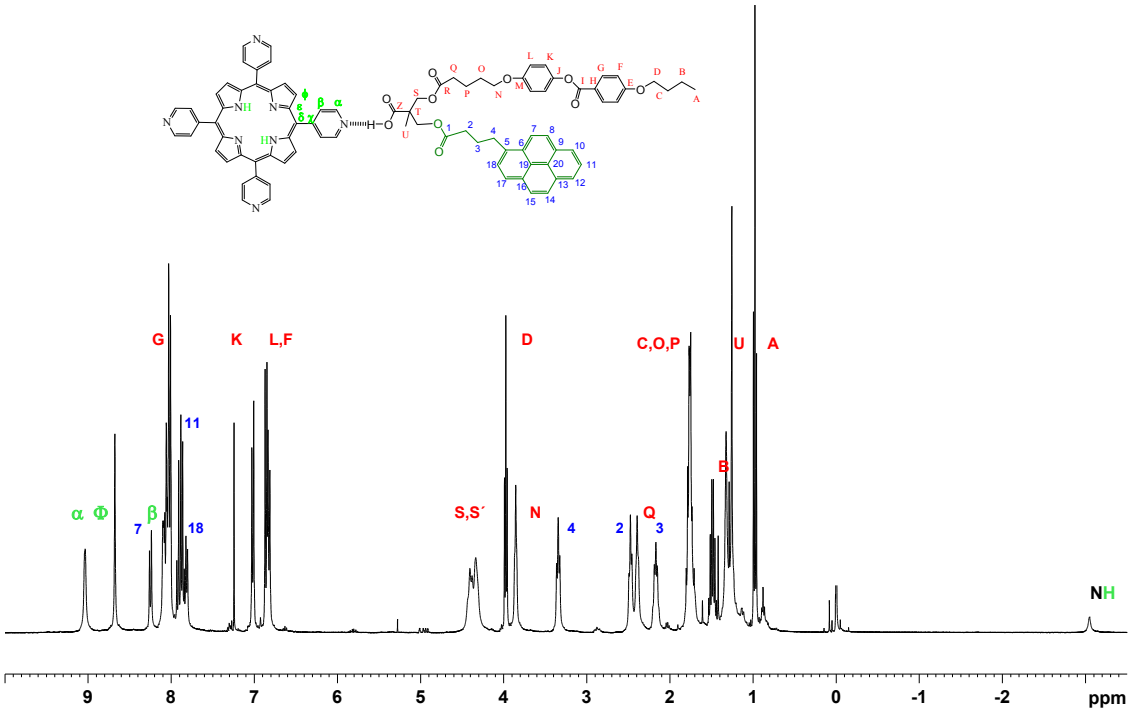


Figure S3. ^{1}H NMR spectrum of complex **TPyP-G1APn.** (500 MHz, $CDCl_3$, 25ºC)

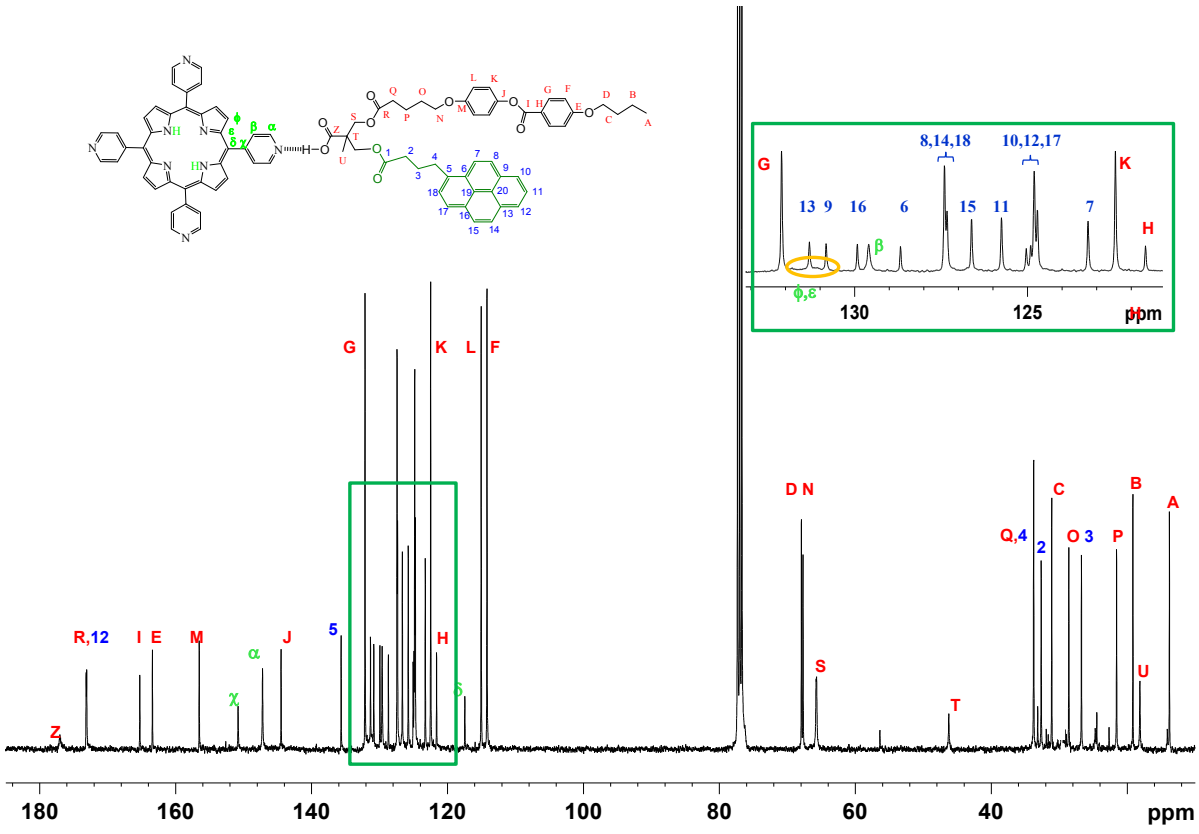


Figure S4. ^{13}C NMR spectrum of complex **TPyP-G1APn.** (500 MHz, $CDCl_3$, 25ºC)

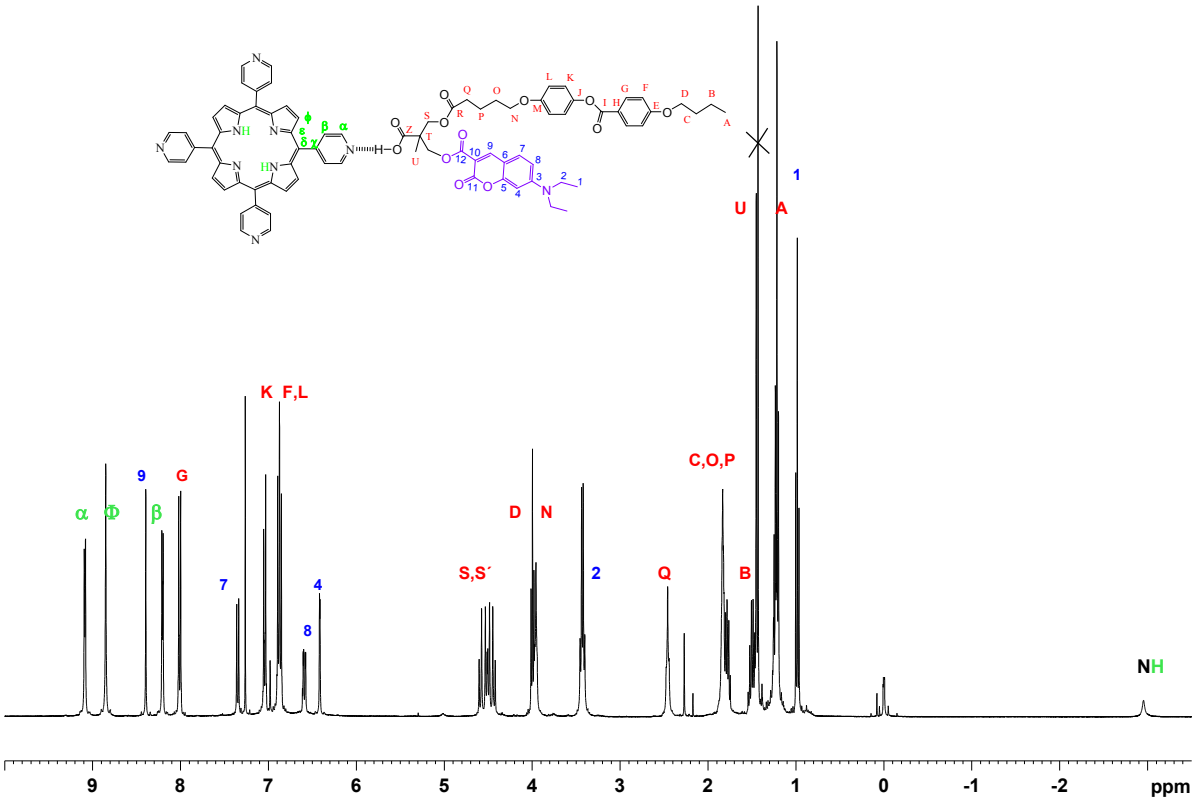


Figure S5. ^{1}H NMR spectrum of complex **TPyP-G1ACou.** (500 MHz, $CDCl_3$, 25ºC)

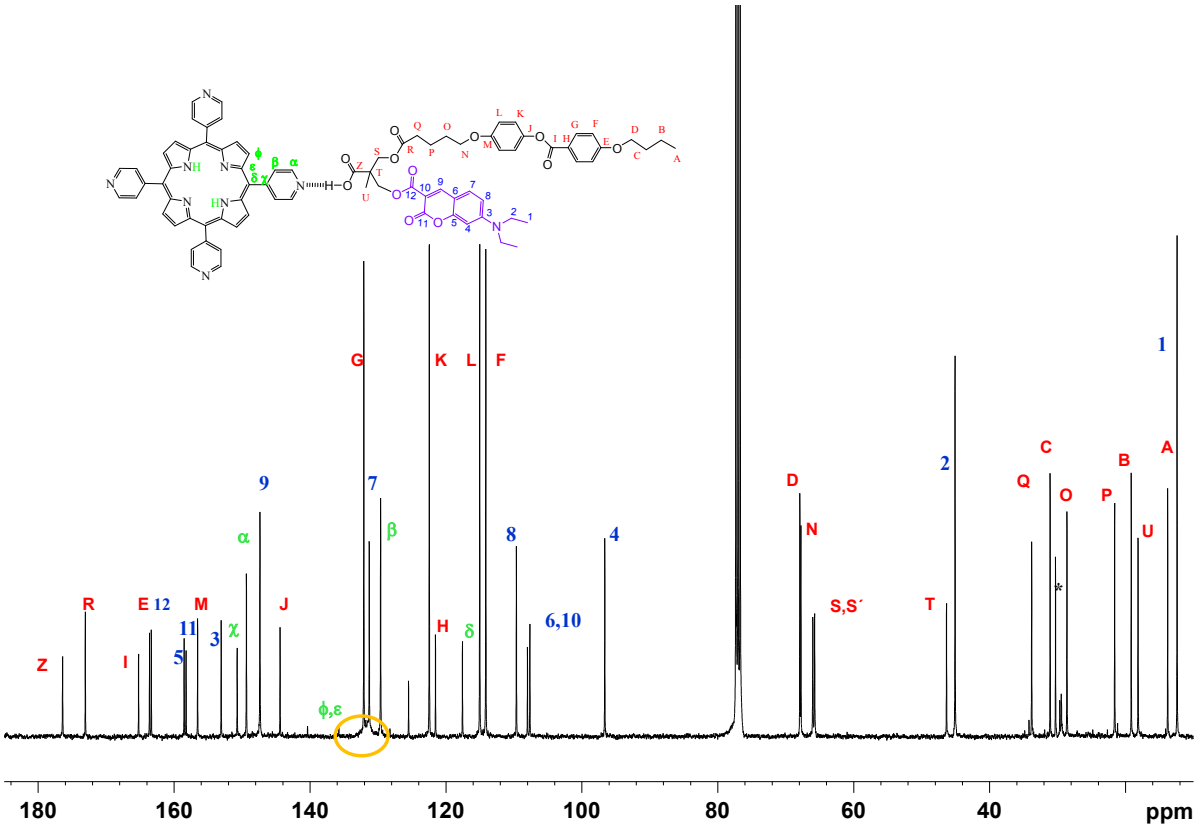


Figure S6. ^{13}C NMR spectrum of complex **TPyP-G1ACou.** (500 MHz, $CDCl_3$, 25ºC)

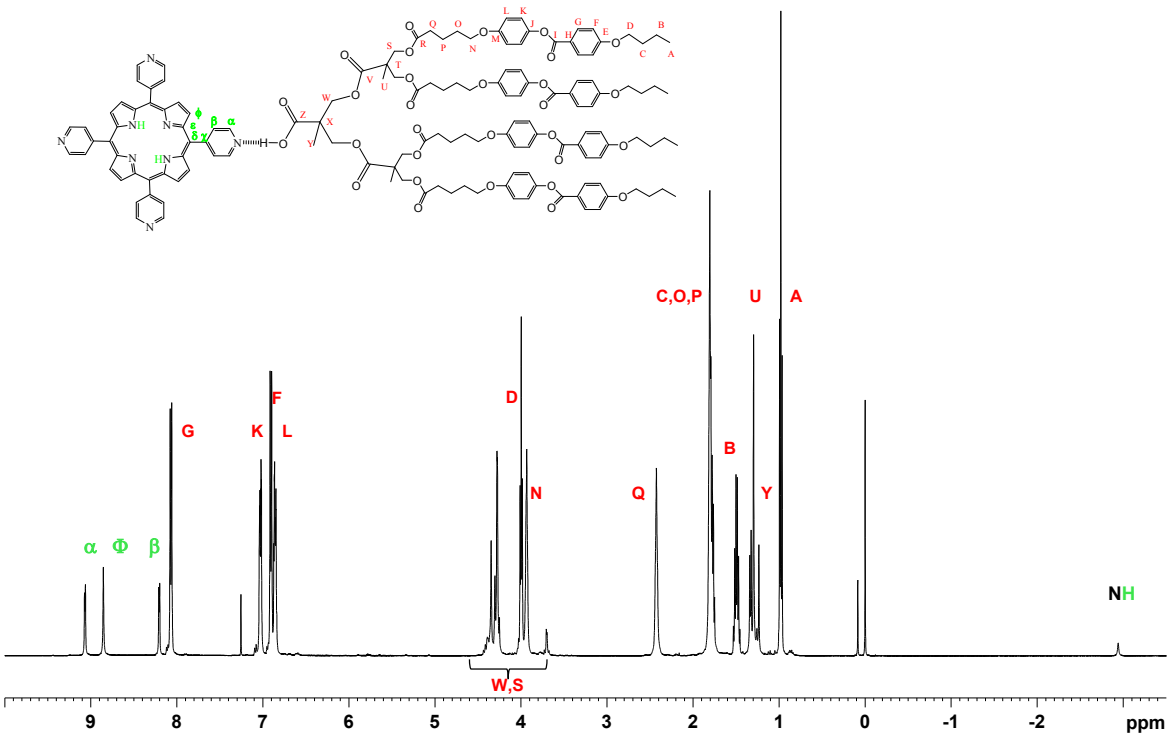


Figure S7. ^{1}H NMR spectrum of complex **TPyP-G2A4.** (500 MHz, $CDCl_3$, 25ºC).

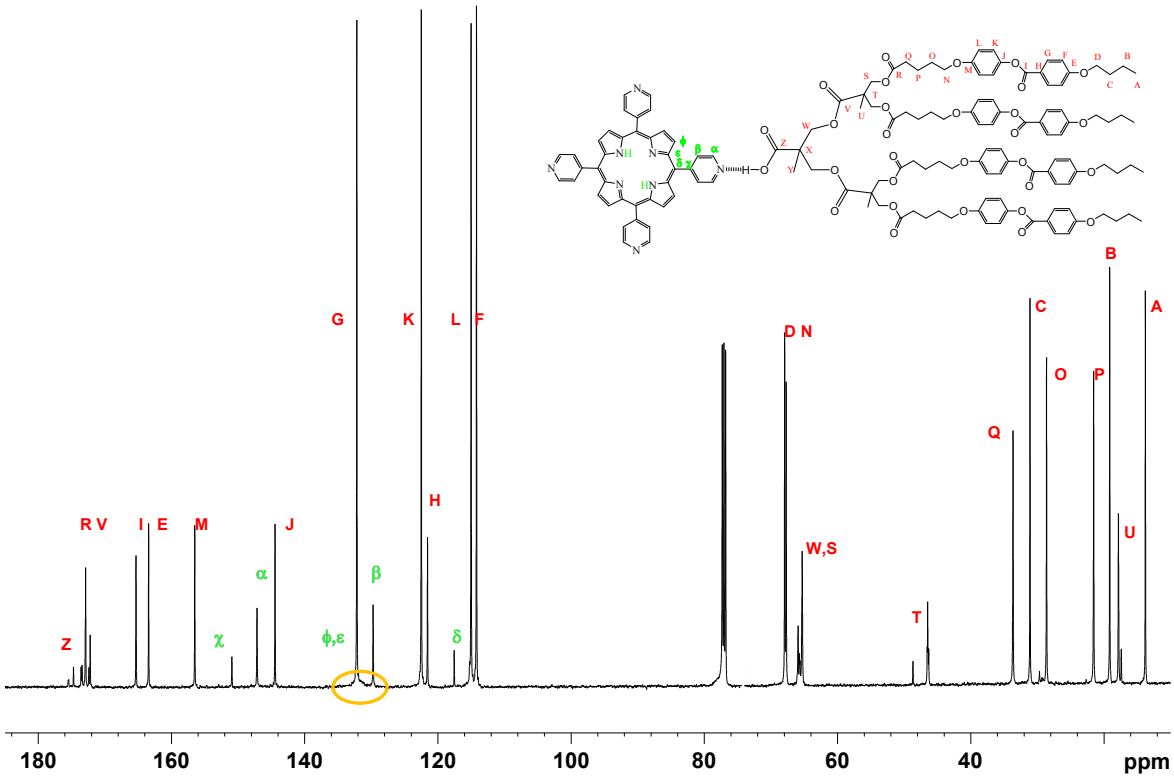


Figure S8. ^{13}C NMR spectrum of complex **TPyP-G2A4.** (500 MHz, $CDCl_3$, 25ºC)

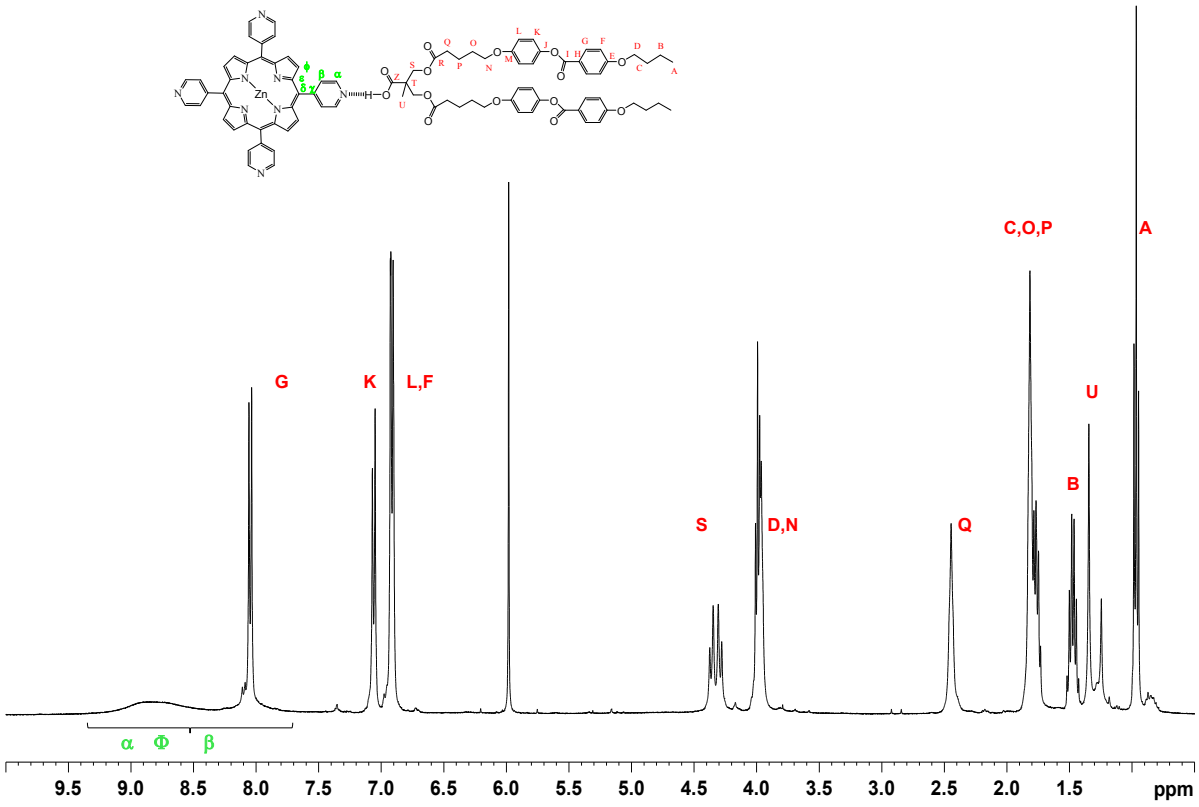


Figure S9. ^{1}H NMR spectrum of complex **ZnTPyP-G1A2.** (500 MHz, $C_2D_2Cl_4$,25ºC)

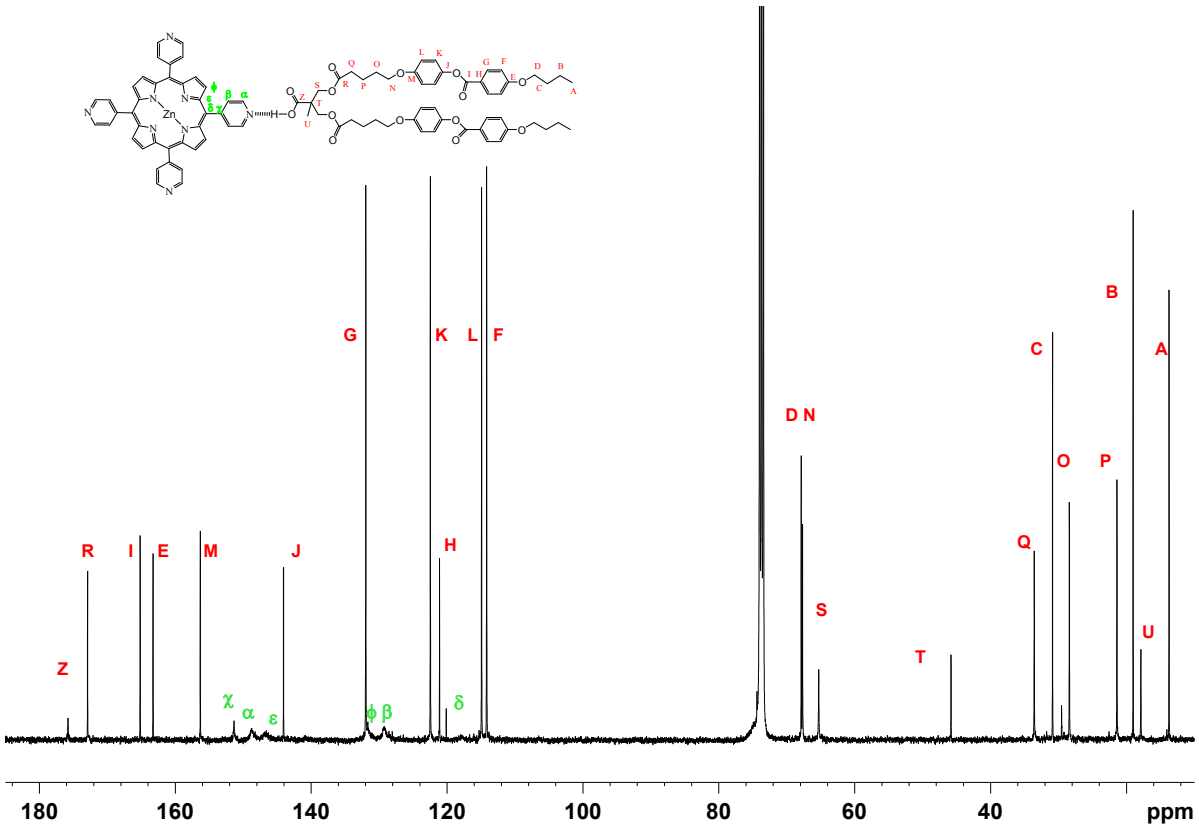


Figure S10. ^{13}C NMR spectrum of complex **ZnTPyP-G1A2.** (500 MHz, $C_2D_2Cl_4$, 25ºC)

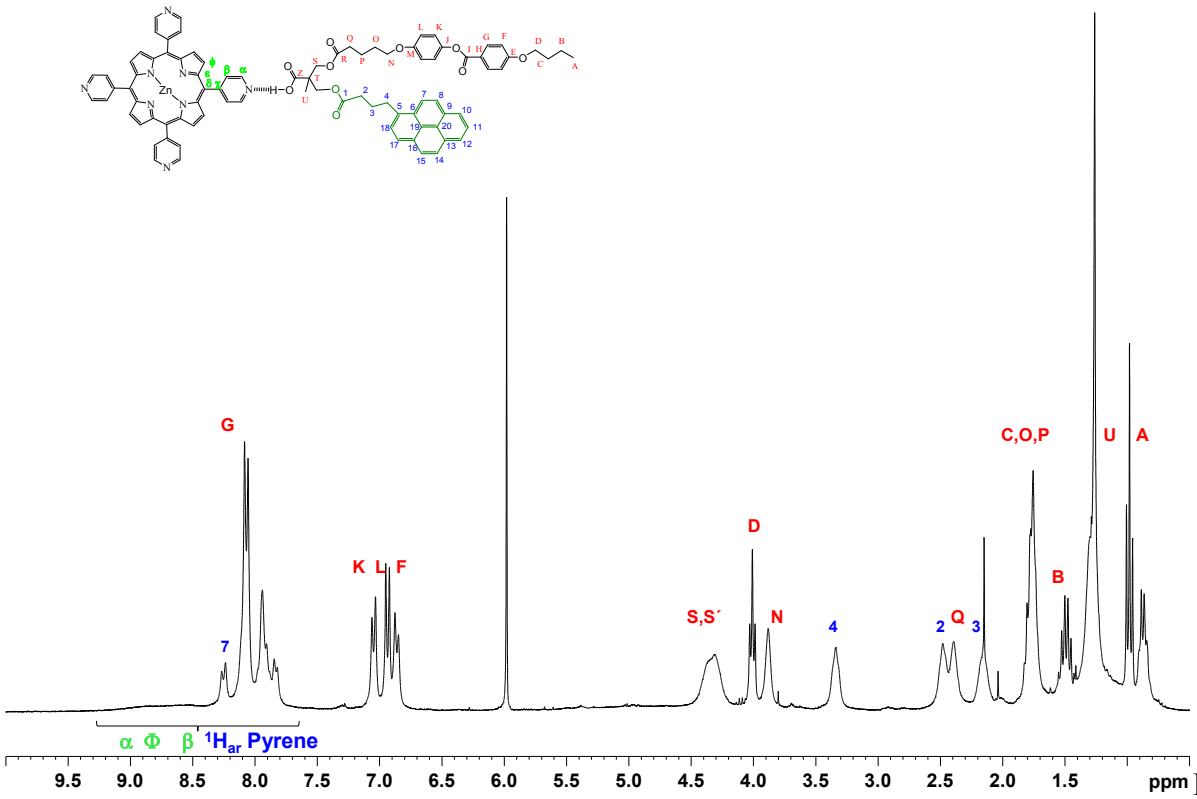


Figure S11. ^{1}H NMR spectrum of complex **ZnTPyP -G1APn.** (500 MHz, $C_2D_2Cl_4$, 25ºC)

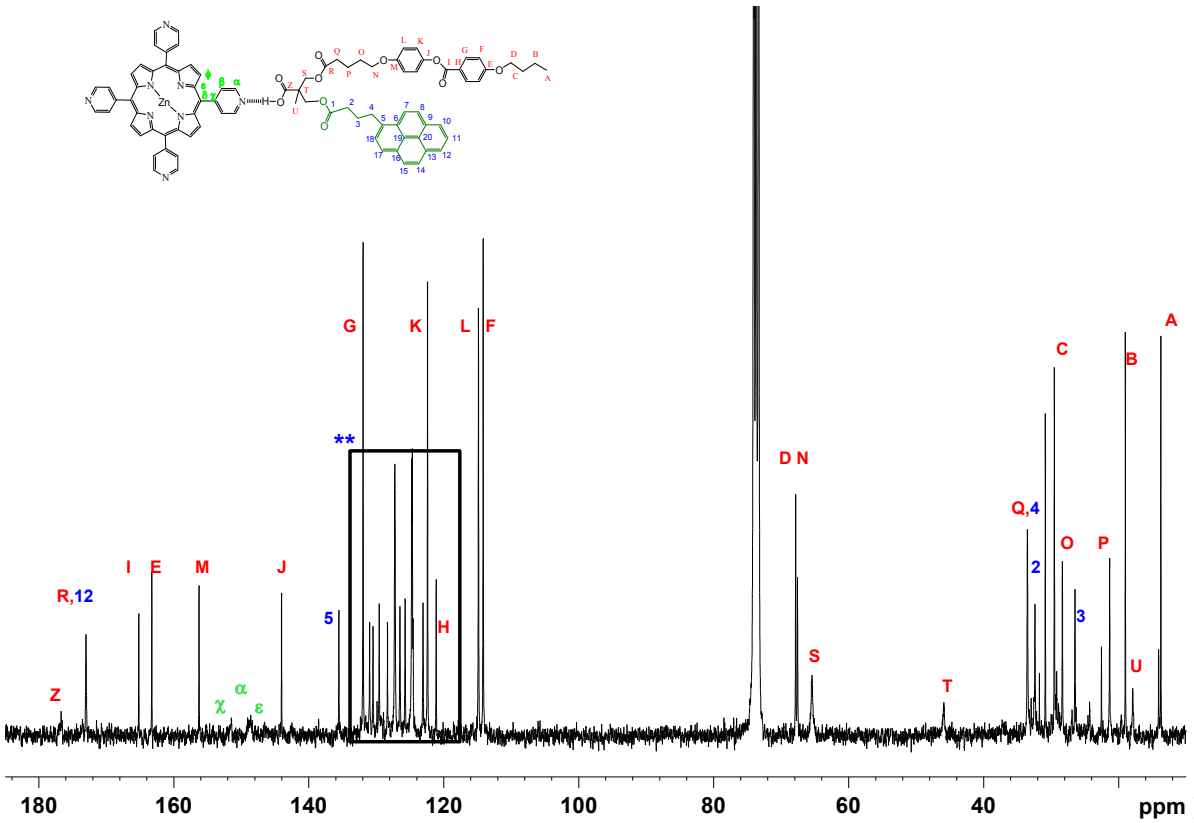


Figure S12. ^{13}C NMR spectrum of complex **ZnTPyP-G1APn.** (500 MHz, $C_2D_2Cl_4$, 25ºC).
**similar to Figure S4

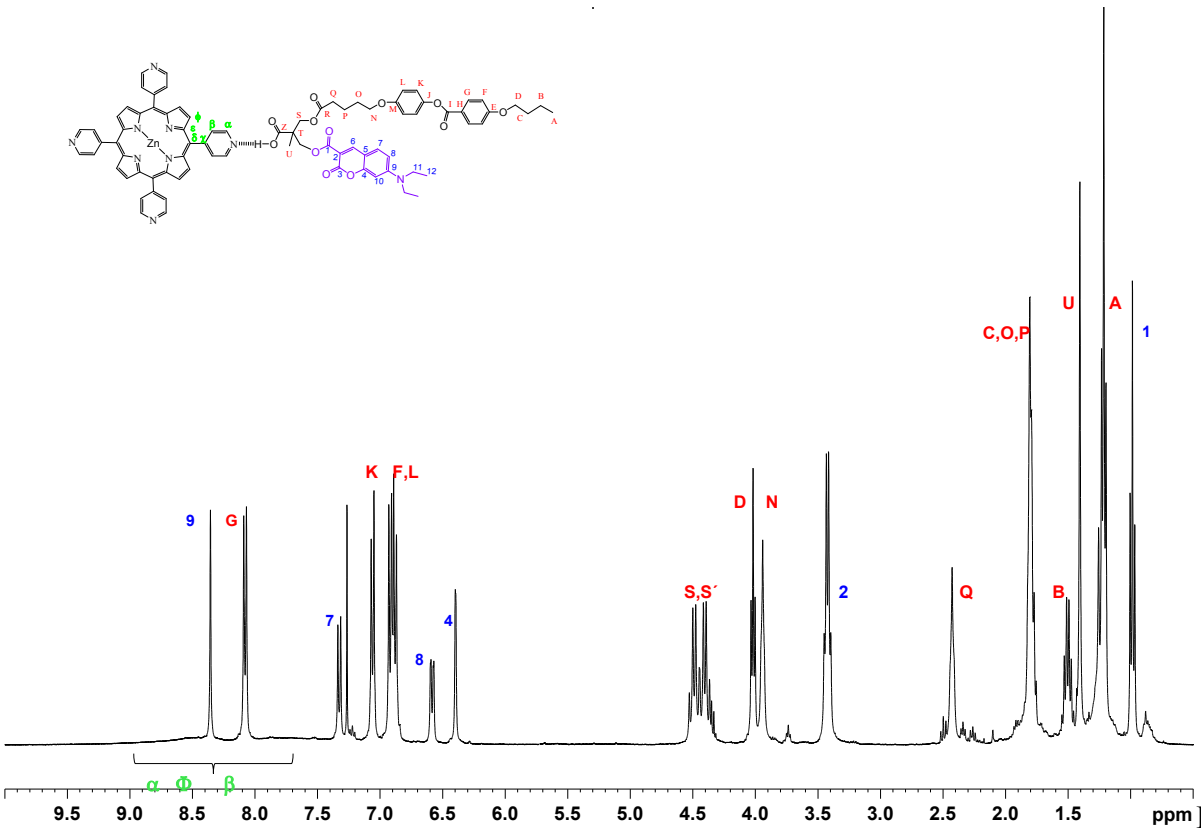


Figure S13. ^{1}H NMR spectrum of complex **ZnTPyP-G1ACou.** (500 MHz, $CDCl_3$, 25ºC)

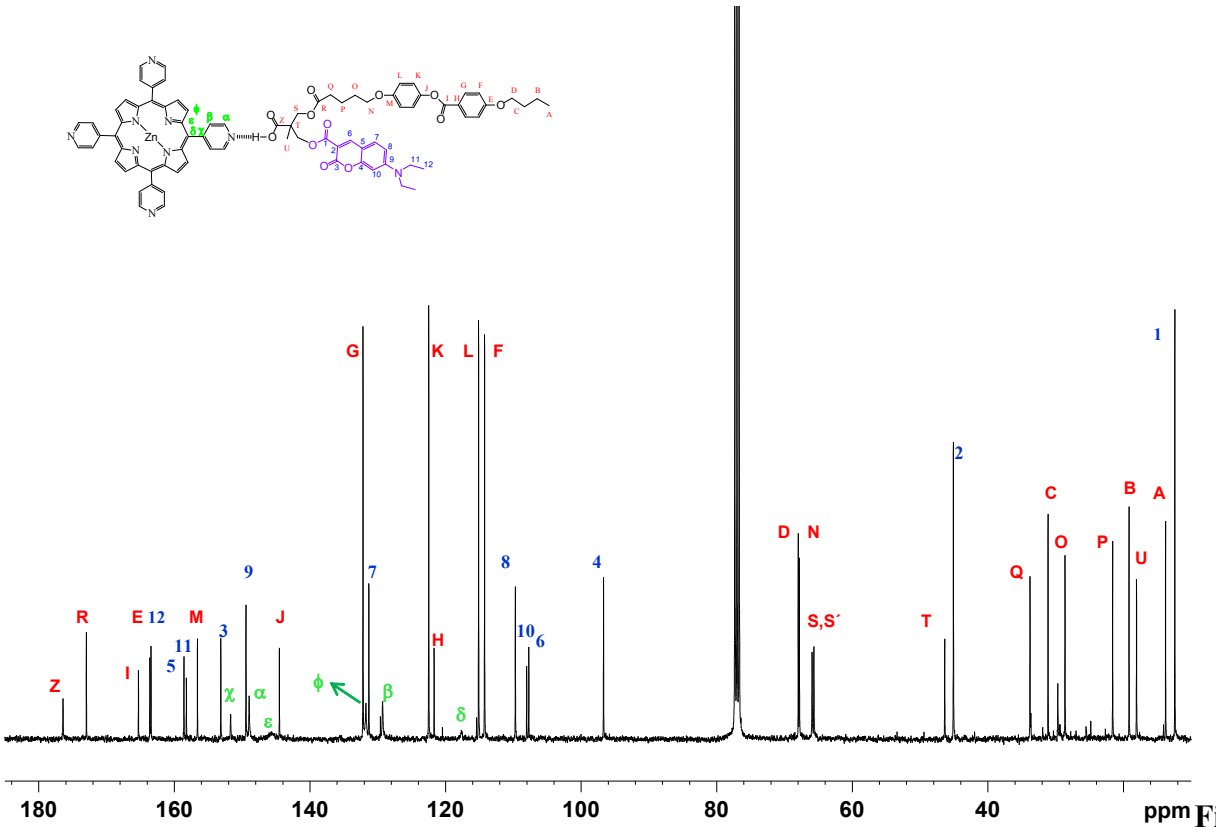


Figure S14. ^{13}C NMR spectrum of complex Zn**TPyP-G1ACou.** (500 MHz, $CDCl_3$, 25ºC)

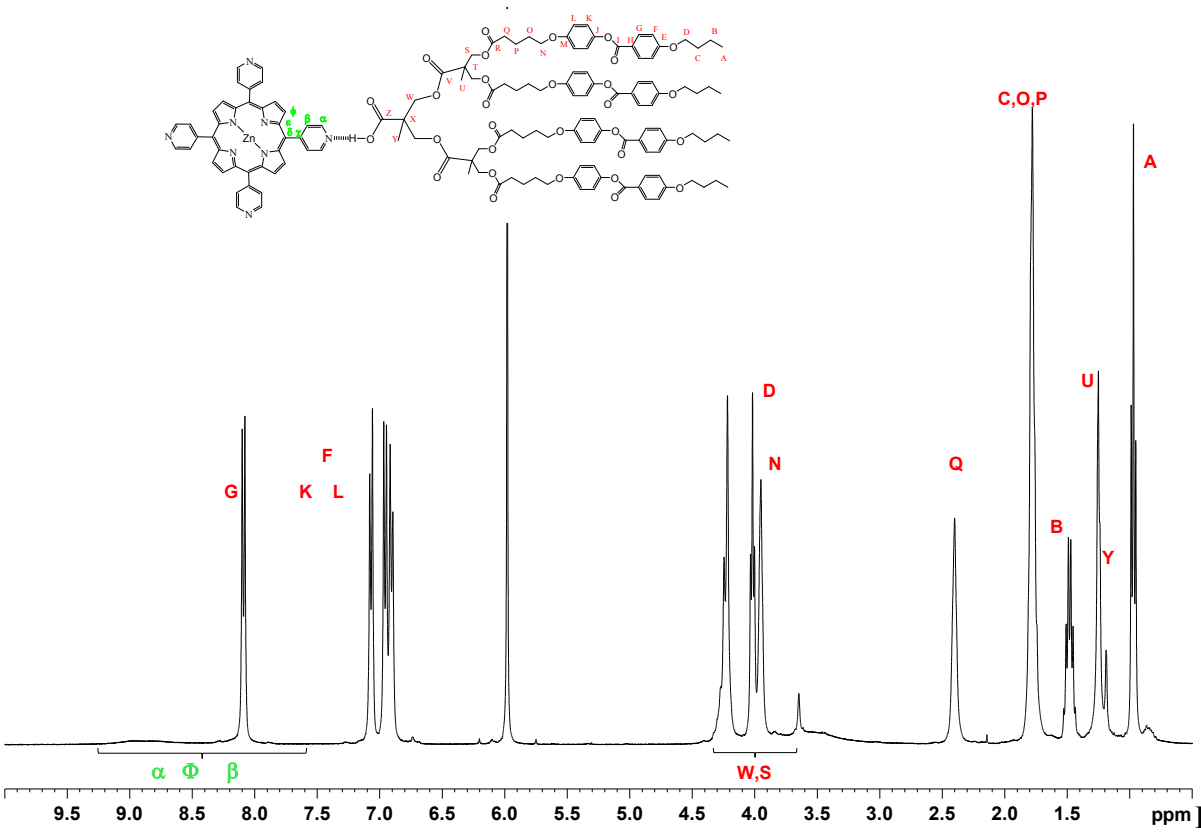


Figure S15. ^{1}H NMR spectrum of complex **ZnTPyP-G2A4.** (500 MHz, $C_2D_2Cl_4$,25ºC)

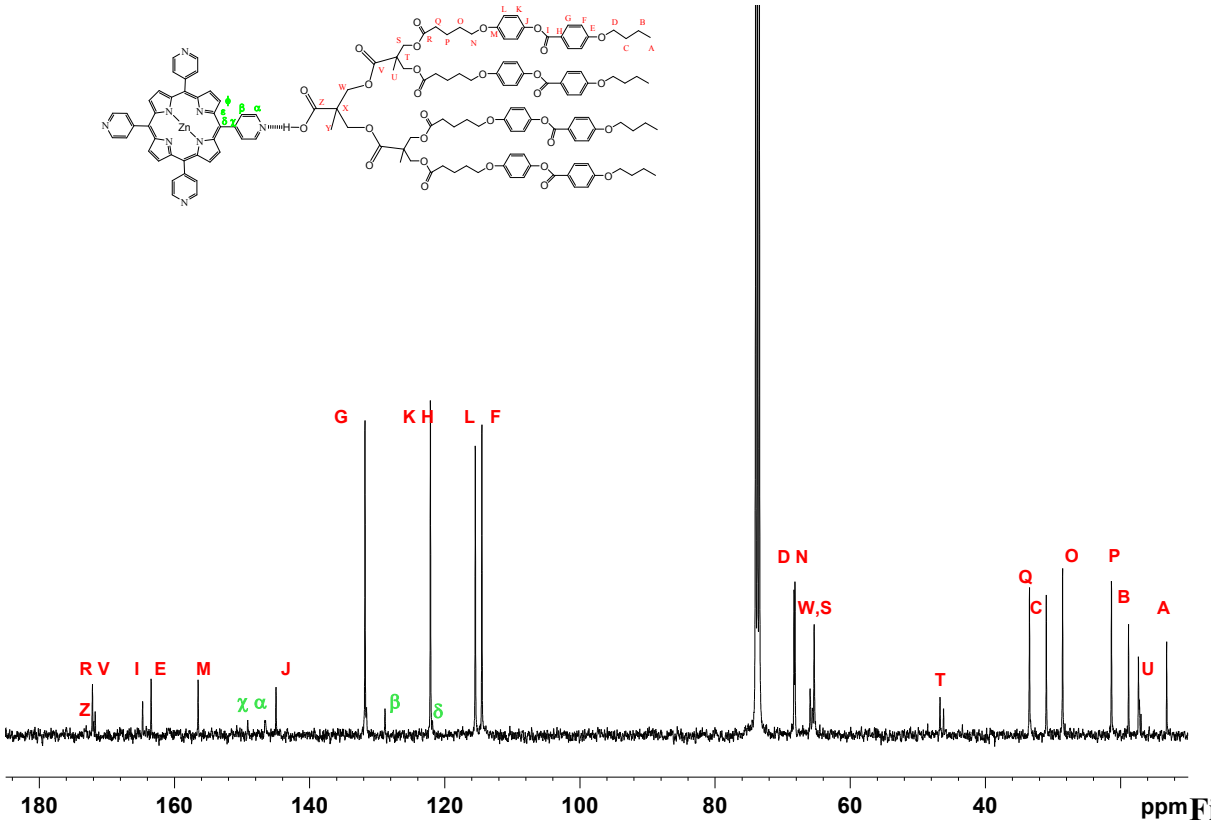


Figure S16. ^{13}C NMR spectrum of complex **ZnTPyP-G2A4.** (500 MHz, $C_2D_2Cl_4$,25ºC)

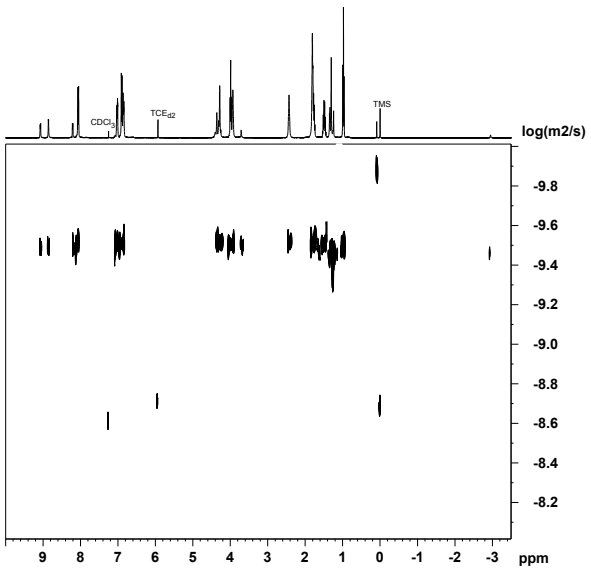


Figure S17 DOSY spectrum ($C_2D_2Cl_4$, at 25 ºC) showing chemical shifts versus diffusion coefficient (logarithmic scale) for complex **TPyP-G2A4**.

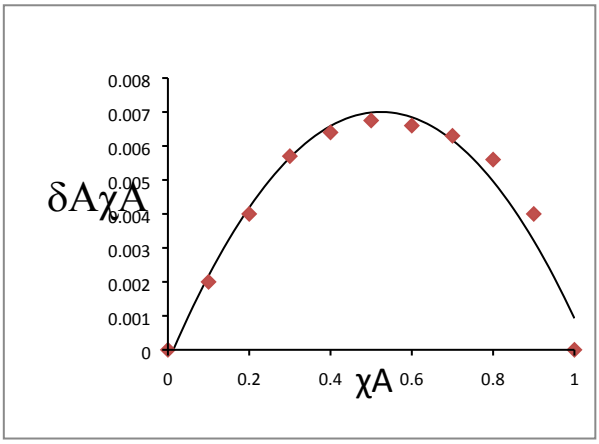


Figure S18. Job´s plot experiment for the formation of complex between **TPYP** and **Ac-G1A2** in $C_2D_2Cl_4$. ^1H NMR spectra were obtained for a series of solutions in which the total concentration of the two species was maintained constant.

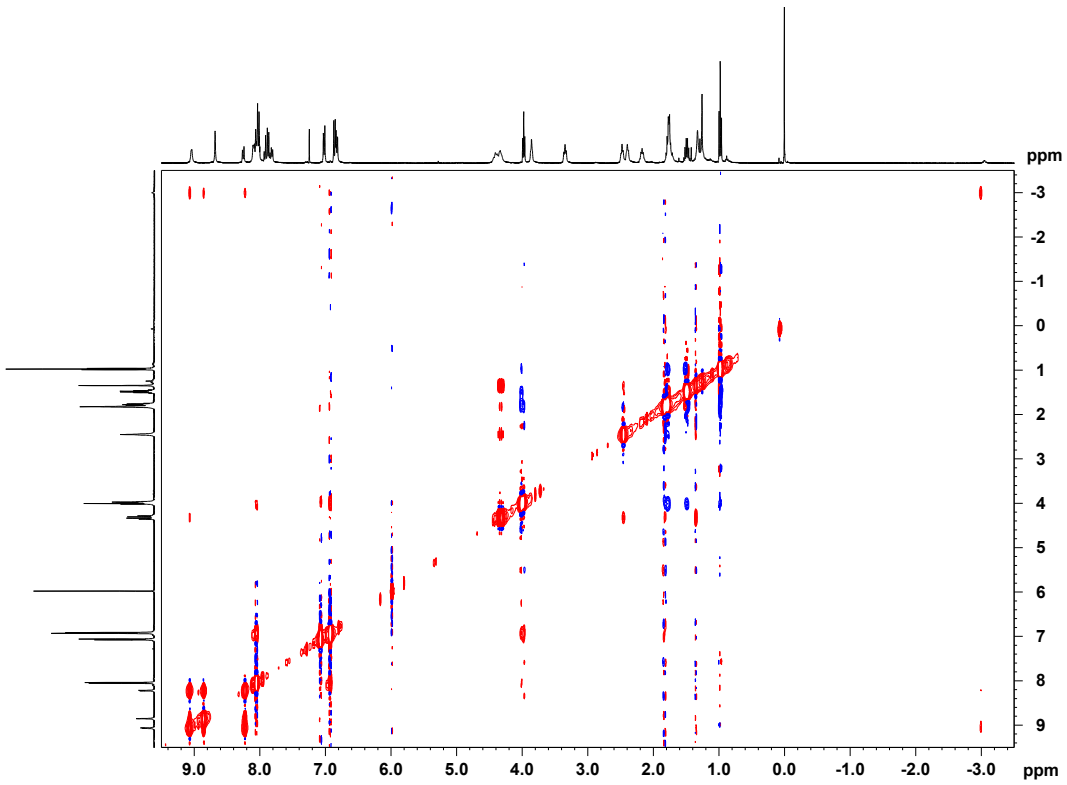


Figure. S19. ^{1}H-^{1}H NOESY spectrum for the complex **TPyP-G1A2.** (500 MHz, $CDCl_3$, 25ºC), t_{mix} = 800 ms.

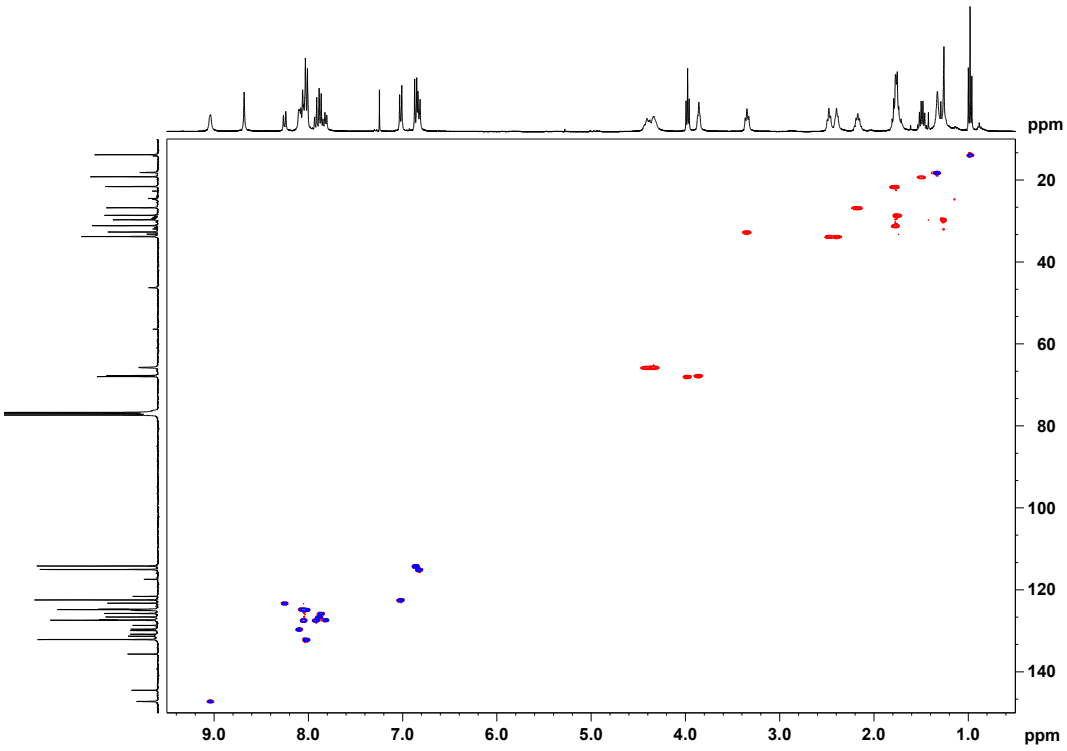


Figure S20. ^{1}H-^{13}C HSQC spectrum of complex **TPyP-G1APn.** (500 MHz, $CDCl_3$, 25ºC)

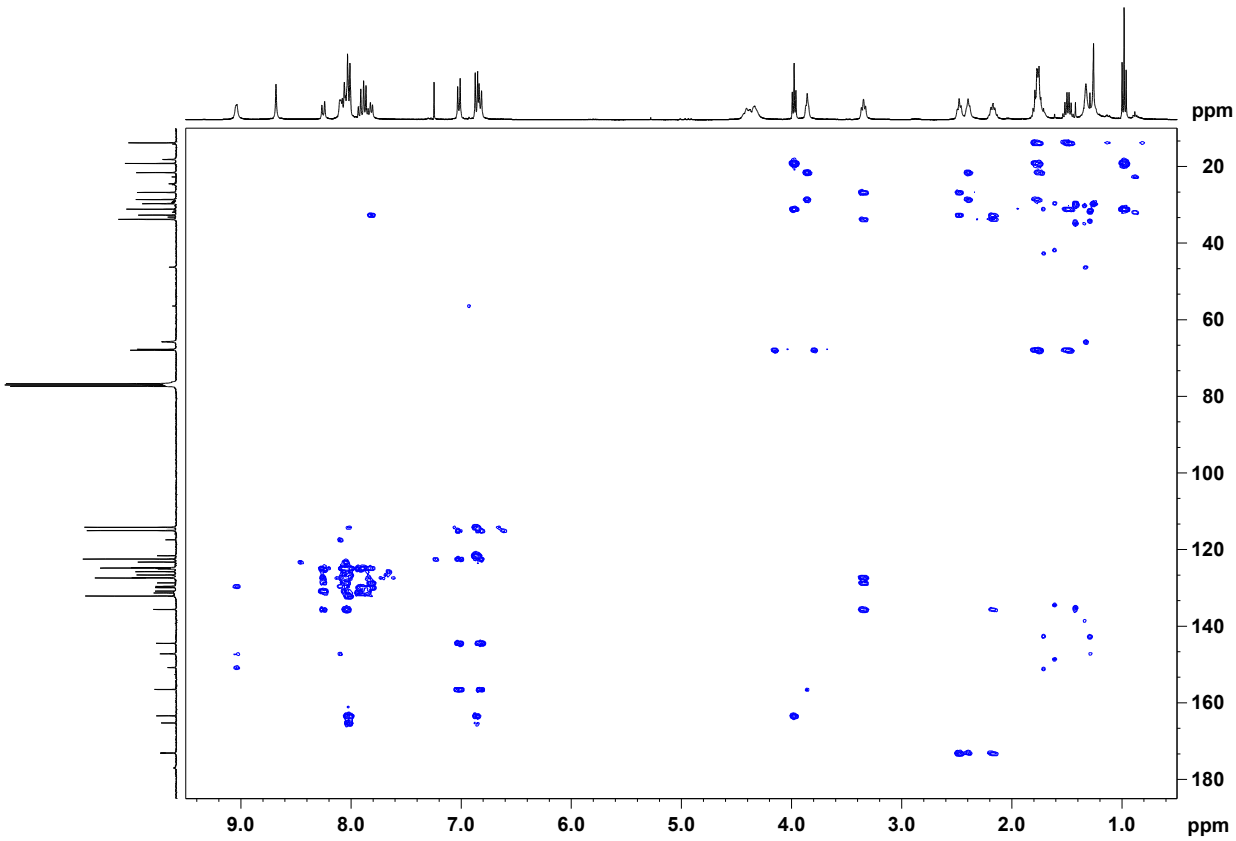
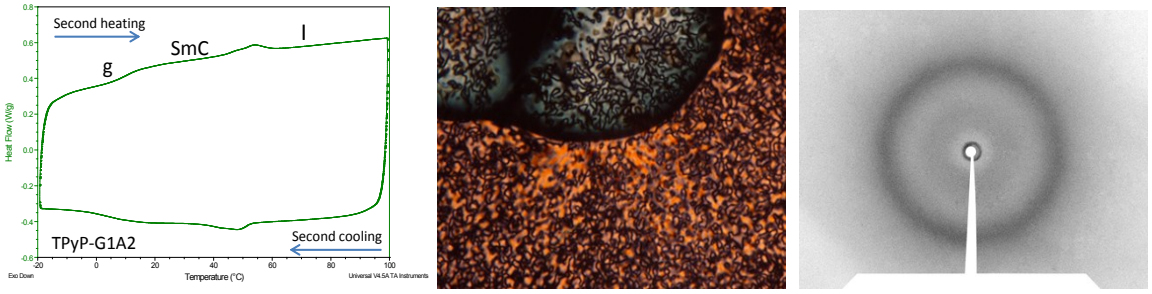


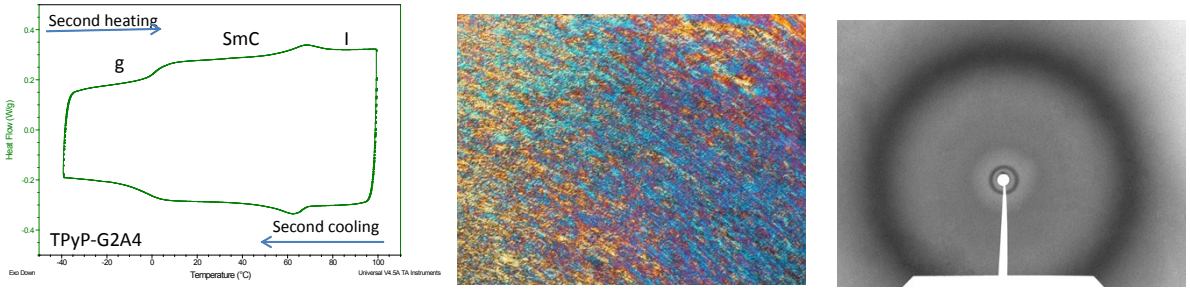
Figure S21. ^{1}H-^{13}C HMBC spectrum of complex **TPyP-G1APn.** (500 MHz, $CDCl_3$, 25ºC)

DSC traces, POM textures and XRD pattern



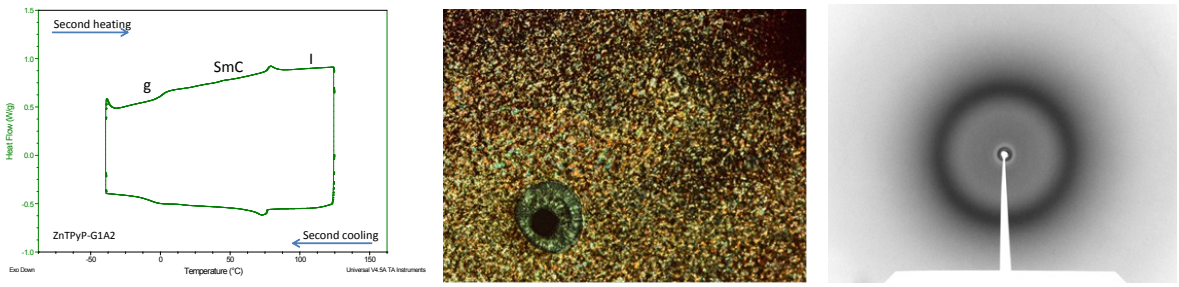
a) b) c)

Figure S22. a) DSC traces of compound **TPyP-G1A2** at a heating and cooling rate of 10 °C min^{-1}; *g*: glass, SmC: smectic C mesophase, I: isotropic liquid. **b)** Microphotographs of optical texture for **TPyP-G1A2** taken at 46 ºC in the cooling process from the isotropic phase observed under the polarizing microscope, (magnification × 50). **c)** Room temperature XRD pattern of **TPyP-G1A2** in the SmC mesophase.



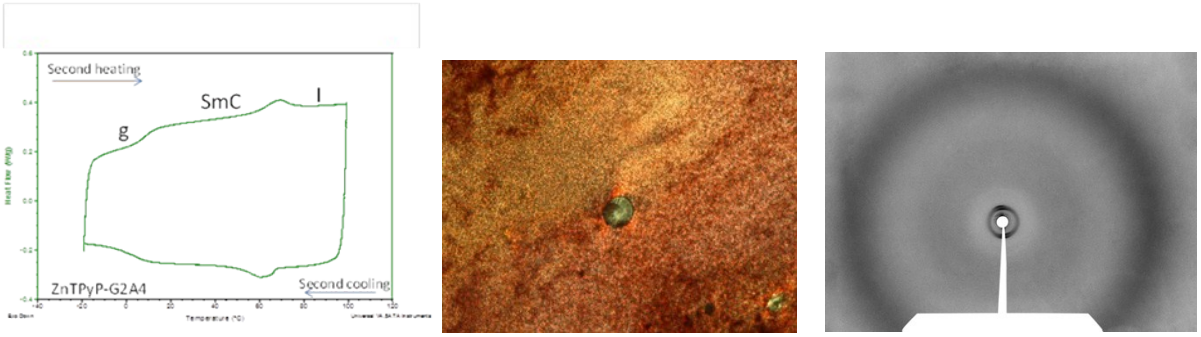
a) b) c)

Figure S23. **a)** DSC traces of compound **TPyP-G2A4** at a heating and cooling rate of 10 °C min^{-1}; *g*: glass, SmC: smectic C mesophase, I: isotropic liquid. **b)** Microphotographs of optical texture for **TPyP-G2A4** taken at 30ºC in the cooling process from the isotropic phase observed under the polarizing microscope, (magnification × 50). **c)** Room temperature XRD pattern of **TPyP-G2A4** in the SmC mesophase.



a) b) c)

Figure S24. a) DSC traces of compound **ZnTPyP-G1A2** at a heating and cooling rate of 10 °C min^{-1}; *g*: glass, SmC: smectic C mesophase, I: isotropic liquid. **b)** Microphotographs of optical texture for **ZnTPyP-G1A2** taken at 29 ºC in the cooling process from the isotropic phase observed under the polarizing microscope (magnification × 20). **c)** Room temperature XRD pattern of **ZnTPyP-G1A2** in the SmC mesophase.



a) b) c)

Figure S25. a) DSC traces of compound **ZnTPyP-G2A4** at a heating and cooling rate of 10 °C min^{-1}; *g*: glass, SmC: smectic C mesophase, I: isotropic liquid **b)** Microphotographs of optical texture for **ZnTPyP-G2A4** taken at 58 ºC in the cooling process from the isotropic phase observed under the polarizing microscope (magnification × 20). **c)** Room temperature XRD pattern of **ZnTPyP-G2A4** in the SmC mesophase.

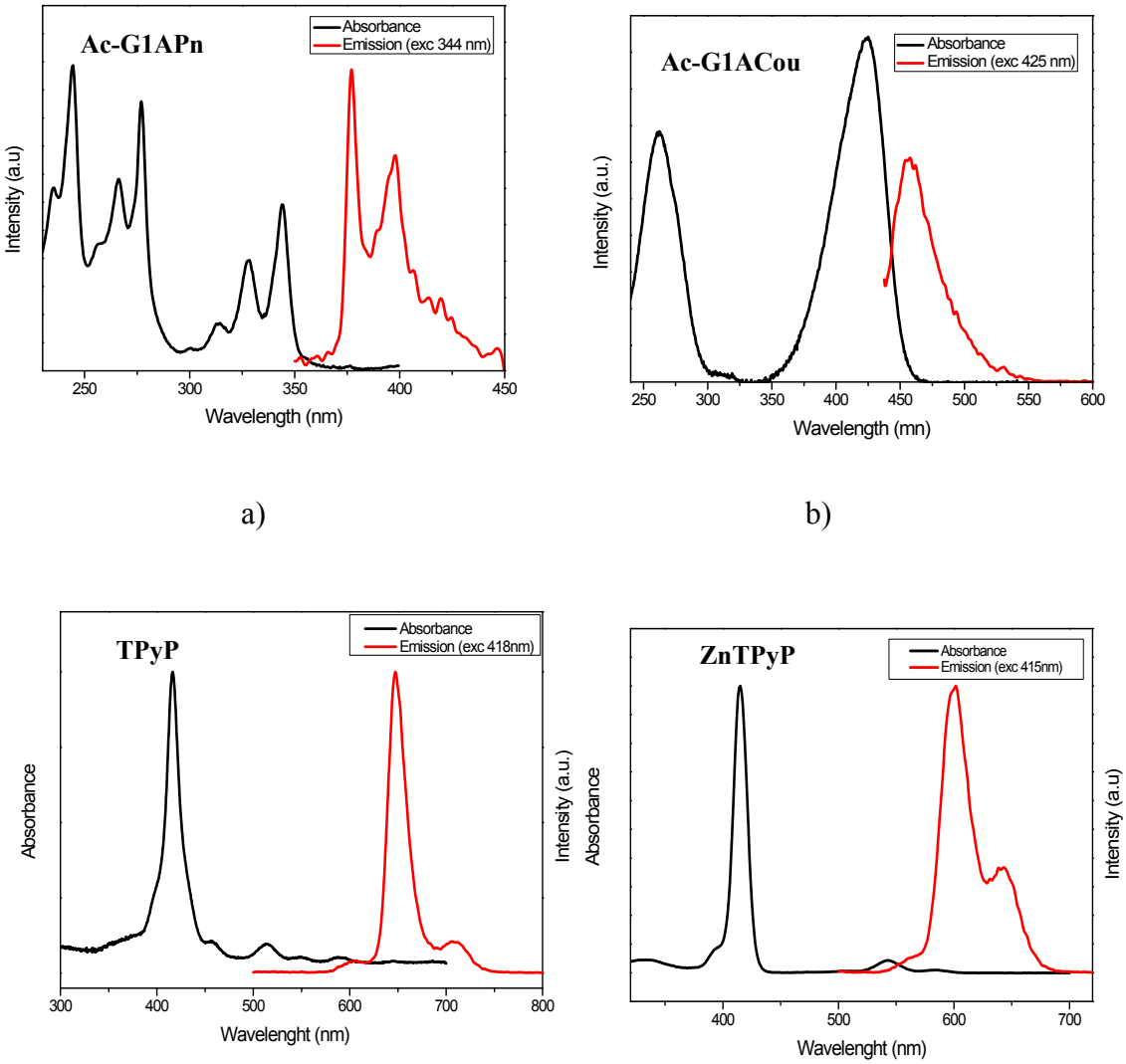


Figure S26. Absorption and fluorescence spectra in solution (CH_2Cl_2) of building blocks: **a) Ac-G1APn, b) Ac-G1APn, c) TPyP** and **d) Zn-TPyP.**