Supporting Information

High hole mobility and light-harvesting in discotic nematic dendrimers prepared via 'click' chemistry

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1. MATERIALS AND CHARACTERIZATION TECHNIQUES

Pyrrole was dried over CaH_2 and vacuum-distilled before use. All other commercially reagents were purchased from Sigma-Aldrich and used as received. Anhydrous THF and DCM were purchased from Scharlab and dried using a solvent purification system. 3,4,5-Tris((11-((2-oxo-2H-chromen-7yl)oxy)undecyl)oxy)benzoic acid (**d$_1$Cou**)[1], 3,4,5-tri(dodecyloxy)benzoic acid (**d$_1$C12**)[2], the alkyne-functionalized Wang resin[3], and the alkyne-functionalized porphyrin core (**ZnP-YNE**)[4], were prepared following previously reported procedures.

FTIR spectra were obtained on a Bruker Vertex 70 FT-IR spectrophotometer using KBr pellets. Solution NMR experiments were carried out on Bruker Avance spectrometers operating at 500 or 400 MHz for ^{1}H and 125 or 100 MHz for ^{13}C, using standard pulse sequences. Chemical shifts are given in ppm relative to TMS and the residual solvent peak was used as internal reference. Elemental analysis was performed using a Perkin-Elmer 2400 microanalyzer. MALDI-TOF MS was performed on an Autoflex mass spectrometer (Bruker Daltonics) using DCTB or dithranol as matrix.

Mesogenic behavior was investigated by polarized-light optical microscopy (POM) using an Olympus BH-2 polarizing microscope fitted with a Linkam THMS600 hot stage.

Thermogravimetric analysis (TGA) was performed using a Q5000IR from TA instruments at heating rate of 10 ºC min^{-1} under a nitrogen atmosphere. Thermal transitions were determined by differential scanning calorimetry (DSC) using a DSC Q2000 from TA instruments with powdered samples (2−5 mg) sealed in aluminum pans. Glass transition temperatures (T_g) were determined at the half height of the baseline jump, and first order transition temperatures were read at the maximum of the corresponding peak.

X-ray diffraction (XRD) was performed with a Ganesha lab instrument equipped with a GeniX-Cu ultralow divergence source producing X-ray photons with a wavelength of 1.54 Å and a flux of $1 \cdot 10^8$ ph·s^{-1}. Scattering patterns were collected using a Pilatus 300 K silicon pixel detector. The beam center and the q range were calibrated using the diffraction peaks of silver behenate. Powdered samples were placed in Lindemann glass capillaries (1 mm diameter).

UV-Vis absorption spectra were recorded on an ATI-Unicam UV4-200 spectrophotometer. Fluorescence measurements were performed using a Perkin-Elmer LS 50B fluorescence spectrophotometer.

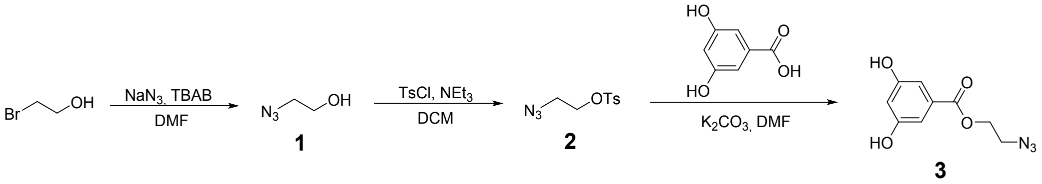
The electrochemical properties were measured using a µ-Autolab ECO-Chemie potentiostat at a scan rate of 100 mV s^{-1} at room temperature. A three-electrode system (a glassy carbon working electrode, Pt counter electrode, and Ag/AgCl reference electrode) was used in all cases. The experiments were carried out under argon in DCM with tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as supporting electrolyte (0.1 M). A ferrocene solution (0.1 M in DCM) was tested by the same procedure to obtain the half-wave potential $E_{1/2,\ FOC}$ in order to correlate all other measurements. The energy of the HOMO level was calculated by the empirical relationship: $E_{HOMO} = -(E_{ox} - E_{1/2,\ FOC} + 4.8)$ eV where E_{ox} is the onset potential for the oxidation wave and $E_{1/2,\ FOC}$ is the oxidation half-wave potential of the FOC. The LUMO was deduced from the optical band gap (ΔE_g), ΔE_g was calculated upon the intersection of the normalized UV-Vis absorption spectrum and the fluorescence spectra. The energy of the LUMO was determined according to the expression: $E_{LUMO} = E_{HOMO} - \Delta E_g$.

Samples for SCLC measurements were prepared in two different ways, either by filling cells prepared by overlapping two glasses with electrodes, or by depositing the active materials by spin-coating on glass substrates. In the first case, the cells were prepared by overlapping one glass with three gold electrodes and one with five ITO electrodes and controlling the spacing between the two substrates with glass spacers. The substrates with ITO electrodes were prepared by photolithography from commercial glass fully covered with ITO (Visiontek 12 Ω/sq, 120 nm thick ITO), while the gold-covered ones were obtained by thermal evaporation. By positioning the two types of electrodes (stripes) perpendicularly to each other, it was possible to obtain cells with 15 independent overlapping areas. The thickness of the cells, measured by interferometry, ranged from 7 to 12 μm. To prepare the sample, the cells were placed on a hot plate, with the compound to be studied on one side, and heated up to 20°C above the melting point, to allow the cell to be filled by capillarity. Because of the high viscosity of the materials, it was necessary to wait around 10-12 hours to observe a complete cell filling. To improve the material alignment, the sample was cooled to RT at 0.1°C/min. On the other hand, the spin-coated samples were obtained at 2000 rpm for 2 minutes on glass substrates with ITO electrodes, from a 10mg/mL solution of the active materials in chloroform. The thickness of the films, measured by a stylus profilometer, was around 100 nm. The samples were then completed by gold counter-electrodes deposited by thermal evaporation (1 Å/s at $5\ 10^{-6}$ mbar base pressure).

The current/voltage data were acquired by either a Keithley 6517A or a Keithley 2636B electrometer, while the low frequency dielectric constants were obtained from capacity measurements performed with a HP 4284A Precision LCR Meter.

2. EXPERIMENTAL PROCEDURES

2.1. Synthesis of the azide precursors

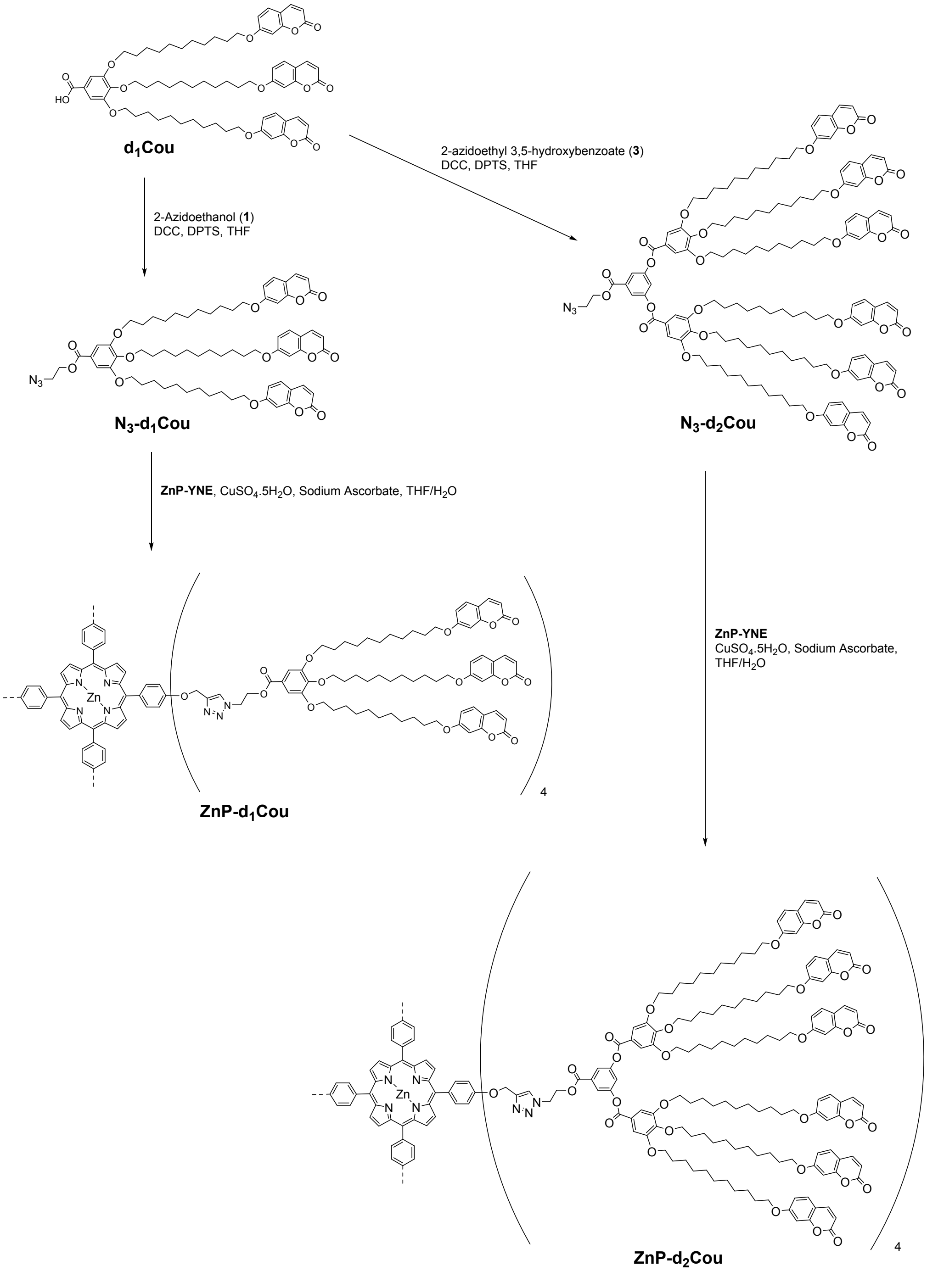


2-Azidoethanol (1). A mixture of 2-bromoethanol (1 mL, 14.11 mmol), sodium azide (1.83 g, 28.22 mmol) and tetrabutylammonium bromide (0.23 g, 0.71 mmol) in DMF (5 mL) was stirred overnight at 100 °C. Then the reaction mixture was poured into water and extracted with diethyl ether. The combined organic phases were washed with brine and dried over anhydrous magnesium sulfate. The solution was filtered and the solvent was removed under reduced pressure. Yield: 83%. IR (KBr, ν, cm^{-1}): 3368 (O-H), 2922 (C-H), 2105 (N_3). ^{1}H NMR ($CDCl_3$, 298K, 400 MHz, δ, ppm): 3.75 (t, *J*= 5.0 Hz, 2H), 3.42 (t, *J*= 5.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 298K, 100 MHz, δ, ppm): 58.42, 49.32.

2-Azidoethyl 4-metylbenzenesulfonate (2). 2-Azidoethanol (**1**) (0.50 g, 5.74 mmol) and triethylamine (1.60 mL, 11.48 mmol) were dissolved in anhydrous DCM (10 mL) and cooled in an ice bath. 4-Toluenesulfonyl chloride (1.64 g, 8.61 mmol) was added dropwise and the reaction mixture was stirred 2 h. After 2 h, the reaction mixture was poured into water and extracted with diethyl ether. The combined organic phases were washed with hydrochloric acid 2M (aq.), sodium bicarbonate 5% (aq.), brine and dried over anhydrous magnesium sulfate. The solution was filtered and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography using DCM as eluent. Yield: 87%. IR (KBr, ν, cm^{-1}): 2111 (N_3), 2920 (C-H), 1142 (S=O). ^{1}H NMR (CD_2Cl_2, 298K, 400 MHz, δ, ppm): 7.82-7.77 (m, 2H), 7.42-7.37 (m, 2H), 4.17-4.09 (m, 2H), 3.52-3.43 (m, 2H), 2.46 (s, 3H). ^{13}C NMR (CD_2Cl_2, 298K, 100 MHz, δ, ppm): 145.91, 141.87, 130.41, 128.28, 68.75, 50.07, 21.81.

2-Azidoethyl 3,5-hydroxybenzoate (3). 2-Azidoethyl 4-metylbenzenesulfonate (**2**) (0.5 g, 2.07 mmol) was added dropwise to a solution of 3,5-dihydroxybenzoic acid (0.29 g, 1.88 mmol) and potassium carbonate (0.39 g, 2.82 mmol) in DMF (10 mL). The mixture was stirred overnight at room temperature. Then the reaction mixture was poured into water and extracted with diethyl ether. The combined organic phases were washed with brine and dried over anhydrous magnesium sulfate. The solution was filtered and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography using DCM as eluent and gradually changing the composition of the eluent to DCM/ethyl acetate (8:2). Yield: 74%. IR (KBr, ν, cm^{-1}): 3400 (O-H), 2922 (C-H), 2100 (N_3), 1701 (C=O), 1610, 1502, 1447 (Ar), 1230, 1011 (C-O). ^{1}H NMR (CD_2Cl_2, 298K, 400 MHz, δ, ppm): 8.26 (s_{broad}, 2H), 7.27 (t, *J*= 2.3 Hz, 1H), 7.00 (d, *J*= 2.3 Hz, 2H), 4.46-4.35 (m, 2H), 3.63-3.50 (m, 2H). ^{13}C NMR (CD_2Cl_2, 298K, 100 MHz, δ, ppm): 166.67, 158.60, 131.83, 108.78, 108.66, 63.80, 50.42.

2.2. Synthesis of coumarin-containing porphyrin-core dendrimers



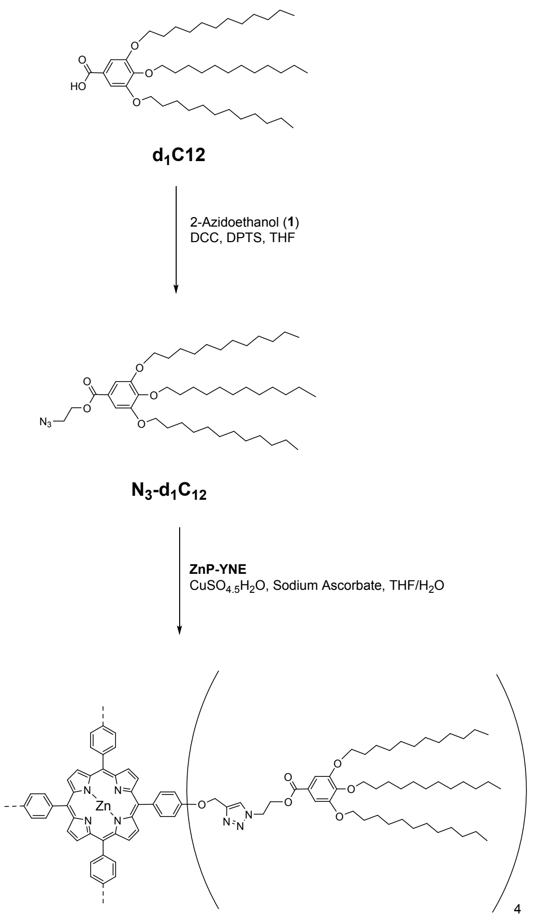
2-Azidoethyl 3,4,5-tris((11-((2-oxo-2*H*-chromen-7-yl)oxy)undecyl)oxy)benzoate (N_3-d_1Cou). Compound **d_1Cou**[1] (0.75 g, 0.67 mmol), 2-azidoethanol (**1**) (88 mg, 1.01 mmol) and 4-(dimethylamino)pyridinium *p*-toluenesulfonate (0.11 g, 0.34 mmol) were dissolved in anhydrous DCM (12 mL). The reaction flask was cooled in an ice bath and flushed with argon, then *N,N'*-dicyclohexylcarbodiimide (0.21 g, 1.01 mmol) was added dropwise. The mixture was stirred at RT for 24 h under argon atmosphere. The white precipitate was filtered off and washed with DCM. The solvent was evaporated and the crude product was purified by flash column chromatography on silica gel using DCM as eluent and gradually changing the composition of the eluent to DCM/ethyl acetate (9:1). Yield: 68%. IR (KBr, ν, cm^{-1}): 3070 (=C-H), 2921 (C-H), 2106 (N_3), 1737 (C=O), 1613, 1471 (Ar), 1231, 1127 (C-O). ^{1}H NMR (CD_2Cl_2, 298K, 400 MHz, δ, ppm): 7.67-7.58 (m, 3H), 7.42-7.33 (m, 3H), 7.27 (s, 2H), 6.86-6.76 (m, 6H), 6.21-6.15 (m, 3H), 4.49-4.41 (m, 2H), 4.08-3.92 (m, 12H), 3.60-3.53 (m, 2H), 1.89-1.64 (m, 12H), 1.53-1.23 (m, 42H). ^{13}C NMR (CD_2Cl_2, 298K, 100 MHz, δ, ppm): 166.43, 163.02, 161.46, 156.54, 153.49, 143.96, 142.97, 129.34, 124.72, 113.38, 113.29, 112.96, 108.36, 101.75, 73.98, 69.69, 69.32, 64.52, 50.67, 30.89, 30.26, 30.18, 30.16, 30.11, 29.97, 29.94, 29.92, 29.89, 29.57, 26.64, 26.53, 26.50. MS (MALDI$^+$, dithranol, m/z): calcd. for $C_{69}H_{87}N_3O_{14}$, 1181.6; found, 1182.1 [M]$^+$, 1205.1 [M+Na]$^+$. Anal. calcd. for $C_{69}H_{87}N_3O_{14}$: C, 70.09%; H, 7.42%; N, 3.55%. Found: C, 70.30%; H, 7.81%; N, 3.16.

2-Azidoethyl 3,5-bis(3,4,5-tris((11-((2-oxo-2*H*-chromen-7-yl)oxy)undecyl)oxy) benzoyloxy)benzoate (N_3-d_2Cou). Compound **d_1Cou**[1] (0.50 g, 0.45 mmol), 2-azidoethyl 3,5-hydroxybenzoate (**3**) (50 mg, 0.22 mmol) and 4-(dimethylamino) pyridinium *p*-toluenesulfonate (70 mg, 0.22 mmol) were dissolved in anhydrous DCM (10 mL). The reaction flask was cooled in an ice bath and flushed with argon, then *N,N'*-dicyclohexylcarbodiimide (0.10 g, 0.49 mmol) was added dropwise. The mixture was stirred at RT for 24 h under argon atmosphere. The white precipitate was filtered off and washed with THF. The solvent was evaporated and the crude product was purified by flash column chromatography on silica gel using DCM as eluent and gradually changing the composition of the eluent to DCM/ethyl acetate (8:2). Yield: 65%. IR (KBr, ν, cm^{-1}): 3075 (=C-H), 2922 (C-H), 2112 (N_3), 1731 (C=O), 1613, 1508 (Ar), 1190, 1122 (C-O). ^{1}H NMR (CD_2Cl_2, 298K, 400 MHz, δ, ppm): 7.85-7.79 (m, 2H), 7.67-7.59 (m, 6H), 7.45-7.31 (m, 11H), 6.86-6.73 (m, 12H), 6.23-6.13 (m, 6H), 4.56-4.44 (m, 2H), 4.13-3.91 (m, 24H), 3.68-3.55 (m, 2H), 1.92-1.64 (m, 24H), 1.61-1.18 (m, 84H). ^{13}C NMR (CD_2Cl_2, 298K, 100 MHz, δ, ppm): 165.14, 165.04, 163.01, 161.44, 156.54, 153.64, 152.17, 143.94, 143.76, 132.46, 129.34, 123.78, 121.54, 121.10, 113.38, 113.28, 112.97, 108.96, 101.76, 74.10, 69.84, 69.32, 64.63, 50.48, 30.93, 30.27, 30.19, 30.16, 30.12, 29.96, 29.92, 29.60, 29.57, 26.66, 26.63, 26.54, 26.51. MS (MALDI$^+$, dithranol, m/z): calcd. for $C_{143}H_{173}N_3O_{30}$, 2412.2; found, 2412.1 [M]$^+$, 2435.1 [M+Na]$^+$. Anal. calcd. for $C_{143}H_{173}N_3O_{30}$: C, 71.15%; H, 7.22%; N, 1.74%. Found: C, 71.03%; H, 6.99%; N, 2.02%.

ZnP-d_1Cou. A Schlenk flask was charged with **ZnP-YNE**[4] (25.2 mg, 0.028 mmol), **N_3-d_1Cou** (200 mg, 0.17 mmol), sodium ascorbate (5.6 mg, 0.028 mmol) and THF (4 mL). Copper (II) sulfate pentahydrate (3.5 mg, 0.014 mmol) was dissolved in water (1 mL) and was added to the reaction. The reaction flask was degassed by three freeze-pump-thaw cycles and flushed with argon. The reaction mixture was stirred at 40 ºC for 48 h. Then, an alkyne-functionalized resin[3] was added under argon flow to remove azide excess and the reaction mixture was stirred for further 24 h. The resin was filtered off, the mixture was diluted with THF and then passed through a short column of aluminum oxide, using THF as eluent, to remove copper salts. The resulting product was carefully precipitated into cold acetone. Yield: 91%. IR (KBr, ν, cm^{-1}): 2923 (C-H), 1730 (C=O), 1612, 1507 (Ar), 1230, 1123 (C-O). ^{1}H NMR (CD_2Cl_2, 298K, 400 MHz, δ, ppm): 8.92 (s, 8H), 8.15-8.05 (m, 8H), 7.93 (s, 4H), 7.56-7.42 (m, 12H), 7.40-7.31 (m, 8H), 7.31-7.11 (m, 20H), 6.75-6.55 (m, 24H), 6.12-5.96 (m, 12H), 5.36 (s, 8H), 4.87-4.79 (m, 8H), 4.79-4.69 (m, 8H), 4.09-3.78 (m, 48H), 1.86-1.56 (m, 48H), 1.52-1.17 (m, 168H). ^{13}C NMR (CD_2Cl_2, 298K, 100 MHz, δ, ppm): 166.23, 162.80, 161.38, 158.61, 156.27, 153.52, 150.85, 144.74, 143.81, 143.17, 136.57, 136.17, 132.28, 129.13, 124.47, 124.17, 120.91, 113.37, 113.14, 112.75, 108.37, 101.56, 74.00, 69.72, 69.18, 63.42, 62.76, 49.96, 30.87, 30.14, 30.07, 29.90, 29.51, 29.45, 26.67, 26.41. MS (MALDI$^+$, DCTB, m/z): calcd. for $C_{334}H_{390}N_{16}O_{60}Zn$, 5648.7; found, 5648.7 $[M]^+$. Anal. calcd. for $C_{334}H_{390}N_{16}O_{60}Zn$: C, 70.95%; H, 6.95%; N, 3.96%. Found: C, 71.20%; H, 6.95%; N, 4.02%.

ZnP-d$_2$Cou. A Schlenk flask was charged with **ZnP-YNE**[4] (15.4 mg, 0.017 mmol), **N$_3$-d$_2$Cou** (250 mg, 0.104 mmol), sodium ascorbate (3.4 mg, 0.017 mmol) and THF (5 mL). Copper (II) sulfate pentahydrate (2.2 mg, 0.009 mmol) was dissolved in water (1 mL) and was added to the reaction. The reaction flask was degassed by three freeze-pump-thaw cycles and flushed with argon. The reaction mixture was stirred at 40 ºC for 48 h. Then, an alkyne-functionalized resin[3] was added under argon flow to remove azide excess and the reaction mixture was stirred for further 24 h. The resin was filtered off, the mixture was diluted with THF and then passed through a short column of aluminum oxide, using THF as eluent, to remove copper salts. The resulting product was carefully precipitated into cold acetone. Yield: 71%. IR (KBr, ν, cm^{-1}): 2917 (C-H), 1732 (C=O), 1610, 1511 (Ar), 1230, 1125 (C-O). ^{1}H NMR (CD_2Cl_2, 298K, 500 MHz, δ, ppm): 9.00-8.77 (m, 8H), 8.22-7.89 (m, 12H), 7.88-7.72 (m, 8H), 7.71-7.05 (m, 76H), 6.92-6.55 (m, 48H), 6.28-5.95 (m, 24H), 5.48-5.36 (m, 8H), 4.98-4.42 (m, 16H), 4.15-3.73 (m, 96H), 1.98-0.95 (m, 432H). ^{13}C NMR (CD_2Cl_2, 298K, 125 MHz, δ, ppm): 165.02, 162.92, 161.45, 156.39, 153.57, 152.20, 150.83, 143.93, 143.73, 136.52, 136.16, 132.12, 129.24, 123.69, 121.70, 121.10, 120.81, 113.38, 113.22, 108.95, 101.64, 74.02, 69.79, 69.24, 63.64, 62.39 (detected by ^{1}H-^{13}C HSQC, H5-C5), 49.51 (detected by ^{1}H-^{13}C HSQC, H2-C2), 30.87, 30.12, 30.06, 29.92, 29.87, 29.55, 29.50, 26.61, 26.50, 26.44. MS (MALDI$^+$, DCTB, m/z): calcd. for $C_{630}H_{734}N_{16}O_{124}Zn$, 10571.1; found, 10571.2 $[M]^+$, 10594.3 $[M+Na]^+$. Anal. calcd. for $C_{630}H_{734}N_{16}O_{124}Zn$: C, 71.52%; H, 6.99%; N, 2.12%. Found: C, 71.13%; H, 6.75%; N, 2.05%.

2.3. Synthesis of dodecyl-containing porphyrin-core dendrimers



ZnP-d$_1$C12

2-Azidoethyl 3,4,5-tris(dodecyloxy)benzoate (N$_3$-d$_1$C12). Compound **d$_1$C12**[2] (0.75 g, 1.11 mmol), 2-azidoethanol (**1**) (0.15 g, 1.67 mmol) and 4-(dimethylamino) pyridinium *p*-toluenesulfonate (0.17 g, 0.55 mmol) were dissolved in anhydrous DCM (10 mL). The reaction flask was cooled in an ice bath and flushed with argon, then *N,N'*-dicyclohexylcarbodiimide (0.34 g, 1.67 mmol) was added dropwise. The mixture was stirred at RT for 24 h under argon atmosphere. The white precipitate was filtered off and washed with DCM. The solvent was evaporated and the crude product was purified by flash column chromatography on silica gel using hexane/ethyl acetate (9:1). Yield: 83%. IR (KBr, ν, cm^{-1}): 2921 (C-H), 2115 (N$_3$), 1735 (C=O), 1608, 1512, 1469 (Ar), 1228, 1126 (C-O). ^{1}H NMR (CD$_2$Cl$_2$, 298K, 500 MHz, δ, ppm): 7.27 (s, 2H), 4.49-4.42 (m, 2H), 4.06-3.95 (m, 6H), 3.63-3.53 (m, 2H), 1.85-1.68 (m, 6H), 1.51-1.20 (m, 54H), 0.88 (t, *J*= 7.0 Hz, 9H). ^{13}C NMR (CD$_2$Cl$_2$, 298K, 125 MHz, δ, ppm): 166.30, 153.37, 142.93, 124.57, 108.28, 73.87, 69.59, 64.33, 50.54, 32.37, 30.76, 30.15, 30.13, 30.09, 30.07, 29.99, 29.82, 29.80, 29.77, 26.52, 26.49, 23.12, 14.29. MS (MALDI$^+$, dithranol, m/z): calcd. for $C_{45}H_{81}N_3O_5$, 743.6; found, 743.7 [M]$^+$, 766.7 [M+Na]$^+$. Anal. calcd. for $C_{45}H_{81}N_3O_5$: C, 72.63%; H, 10.97%; N, 5.65%. Found: C, 72.33%; H, 10.83%; N, 5.72.

ZnP-d$_1$C12. A Schlenk flask was charged with **ZnP-YNE**[4] (70.7 mg, 0.079 mmol), **N$_3$-d$_1$C12** (0.25 g, 0.336 mmol), sodium ascorbate (15.7 mg, 0.079 mmol) and THF (3 mL). Copper (II) sulfate pentahydrate (9.9 mg, 0.040 mmol) was dissolved in water (1 mL) and was added to the reaction. The reaction flask was degassed by three freeze-pump-thaw cycles and flushed with argon. The reaction mixture was stirred at 40 °C for 48 h. Then, an alkyne-functionalized resin[3] was added under argon flow to remove azide excess and the reaction mixture was stirred for further 24 h. The resin was filtered off, the mixture was diluted with THF and then passed through a short column of aluminum oxide, using THF as eluent, to remove copper salts. The resulting product was carefully precipitated into cold methanol. Yield: 82%. IR (KBr, ν, cm^{-1}): 2924 (C-H), 1732 (C=O), 1610, 1509, 1470 (Ar), 1232, 1125 (C-O). ^{1}H NMR (CD_2Cl_2, 298K, 500 MHz, δ, ppm): 8.97-8.91 (m, 8H), 8.12-8.06 (m, 8H), 7.76-7.68 (m, 4H), 7.29-7.21 (m, 8H), 7.20 (s, 2H), 5.02-4.85 (m, 8H), 4.72-4.56 (m, 16H), 4.09-3.88 (m, 24H), 1.86-1.62 (m, 24H), 1.50-1.10 (m, 216H), 0.89-0.73 (m, 54H). ^{13}C NMR (CD_2Cl_2, 298K, 125 MHz, δ, ppm): 166.03, 158.34, 153.40, 150.86, 144.42, 143.18, 136.59, 136.05, 132.14, 124.25, 123.58, 120.83, 113.21, 108.30, 100.45, 73.88, 69.62, 63.11, 62.32, 49.70, 32.31, 30.75, 30.11, 30.06, 29.96, 29.84, 29.78, 26.55, 26.47, 23.07, 14.27. MS (MALDI^{+}, DCTB, m/z): calcd. for $C_{238}H_{366}N_{16}O_{24}Zn$, 3896.7; found, 3896.9 $[M]^{+}$. Anal. calcd. for $C_{238}H_{366}N_{16}O_{24}Zn$: C, 73.28%; H, 9.46%; N, 5.74%. Found: C, 73.00%; H, 9.49%; N, 6.02%.

3. SUPPLEMENTARY FIGURES

3.1. NMR Spectra

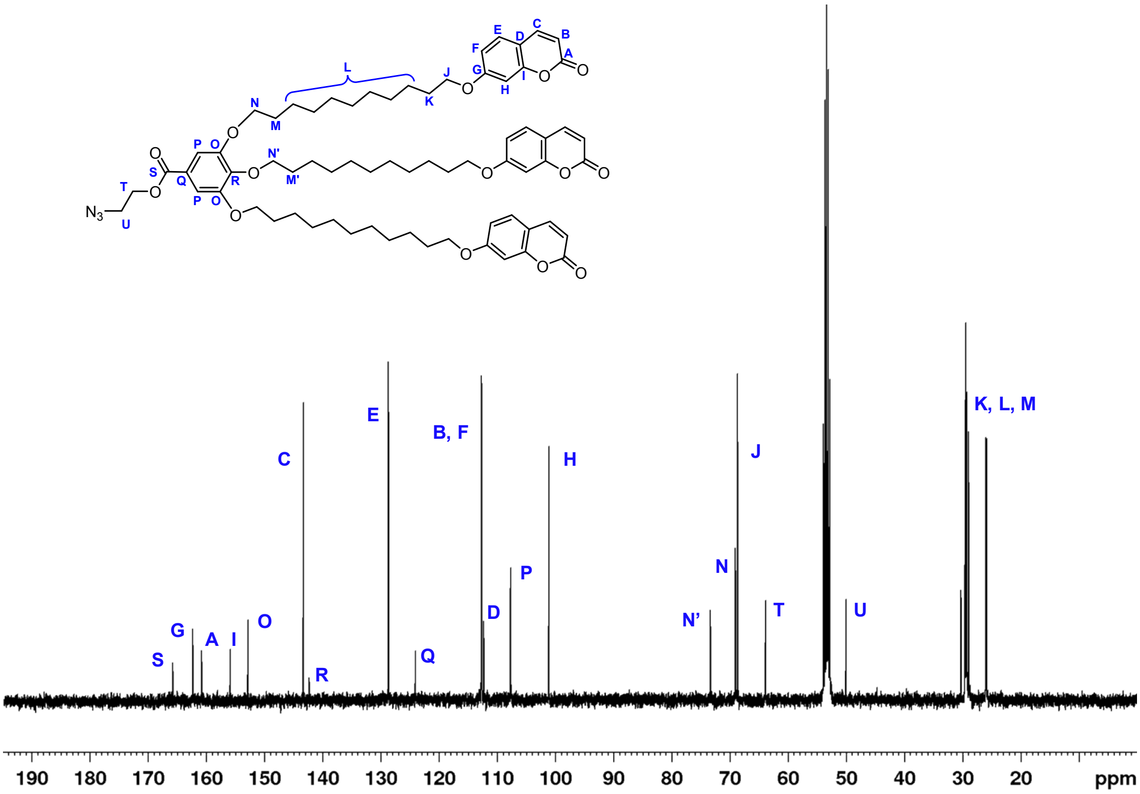


Figure S1. ^{13}C NMR spectrum (100 MHz, 298K, CD_2Cl_2) of **N_3-d$_1$Cou**

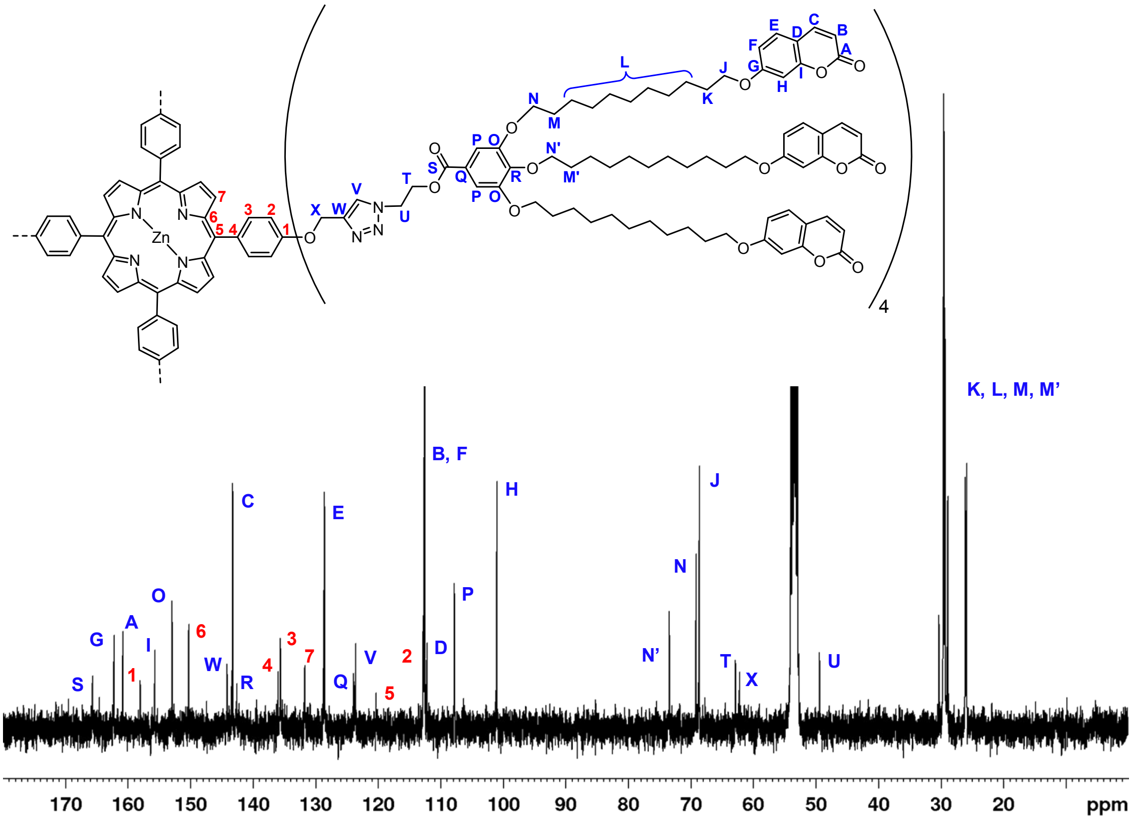


Figure S2. ^{13}C NMR spectrum (100 MHz, 298K, CD_2Cl_2) of **ZnP-d$_1$Cou**

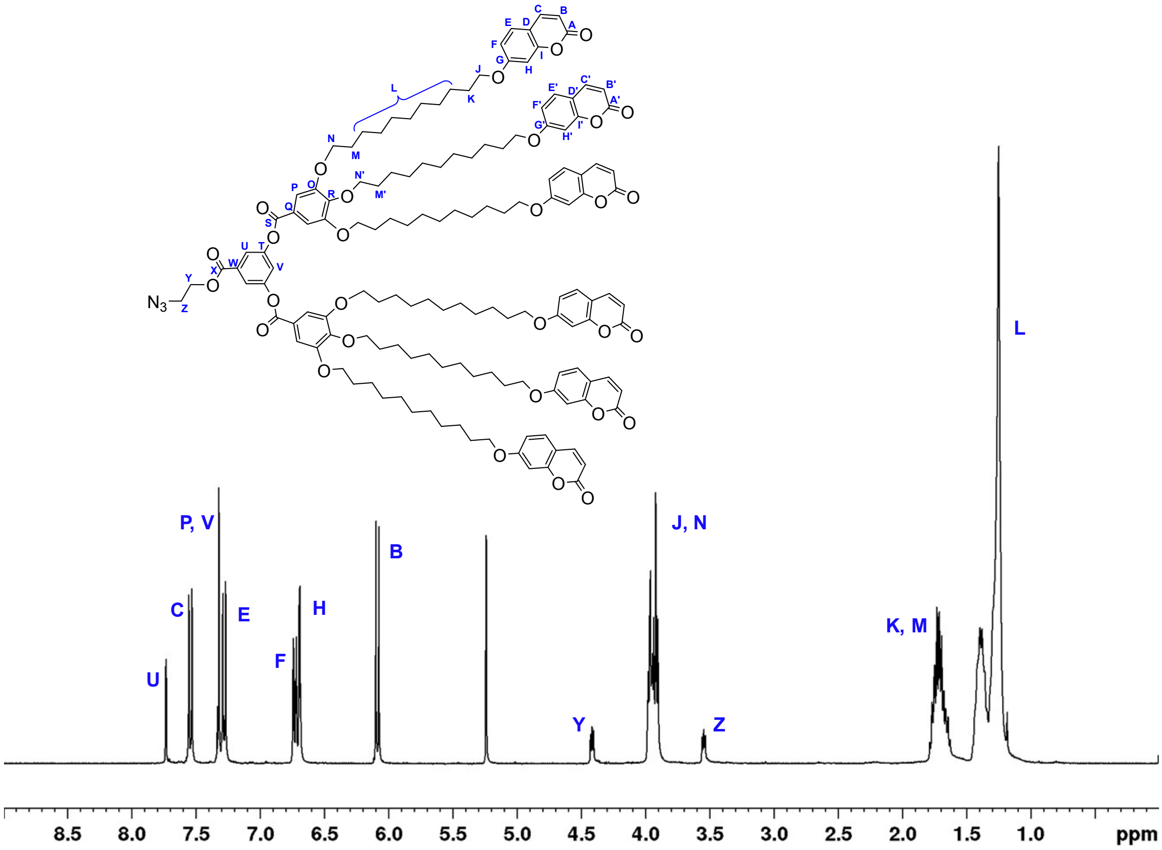


Figure S3. ^{1}H NMR spectrum (400 MHz, 298K, CD_2Cl_2) of **N_3-d_2Cou**

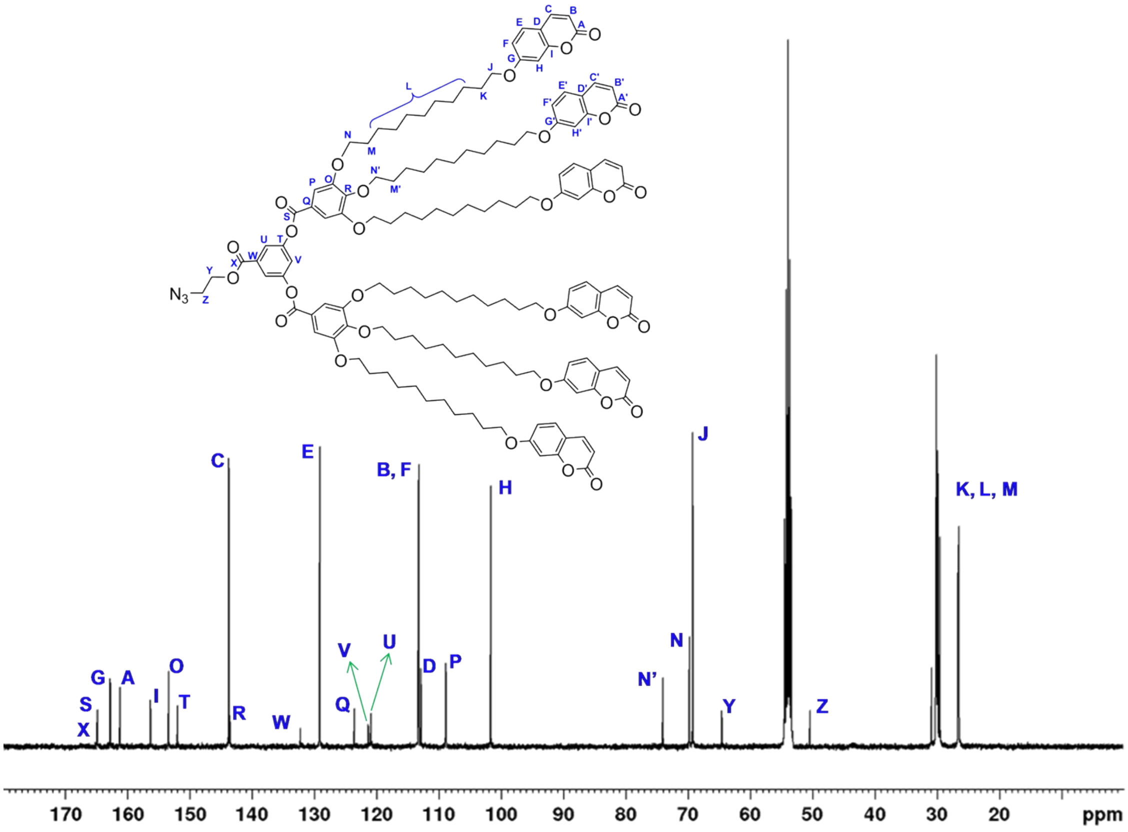


Figure S4. ^{13}C NMR spectrum (100 MHz, 298K, CD_2Cl_2) of **N_3-d_2Cou**

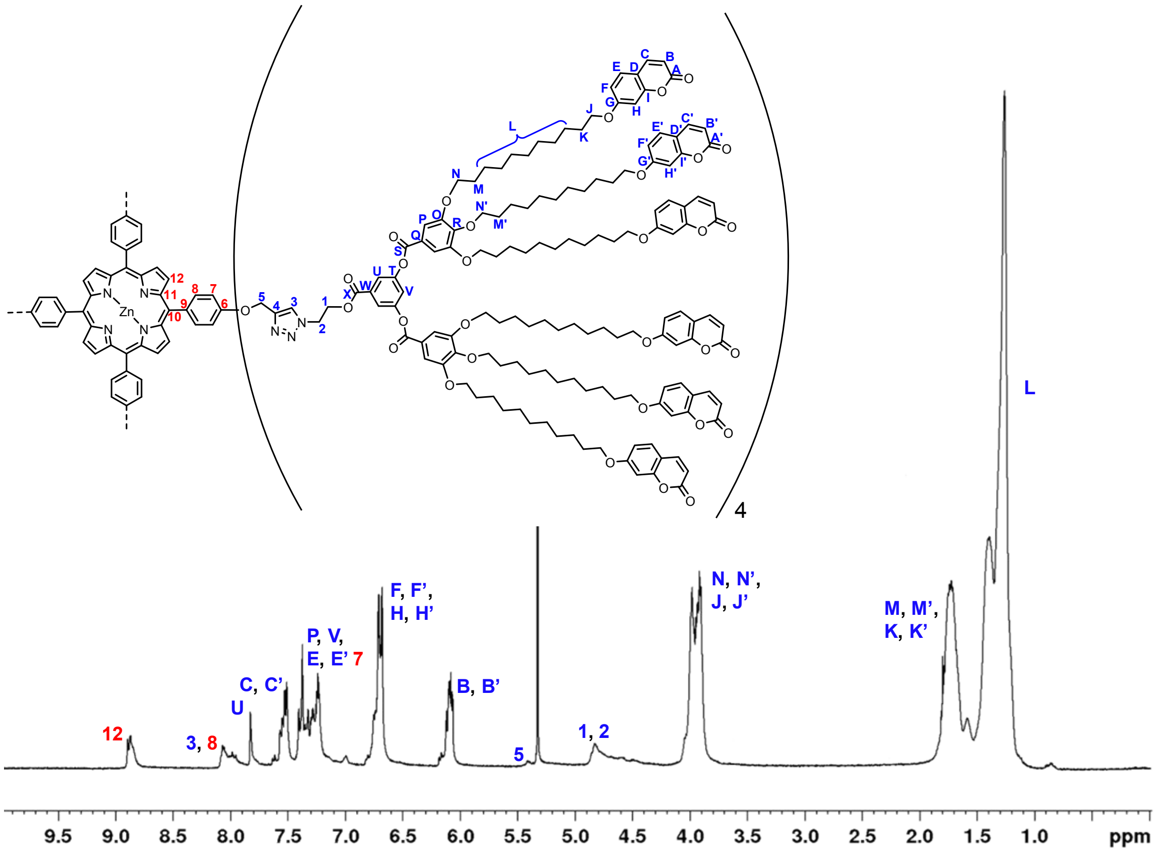


Figure S5. ^{1}H NMR spectrum (500 MHz, 298K, CD_2Cl_2) of **ZnP-d$_2$Cou**

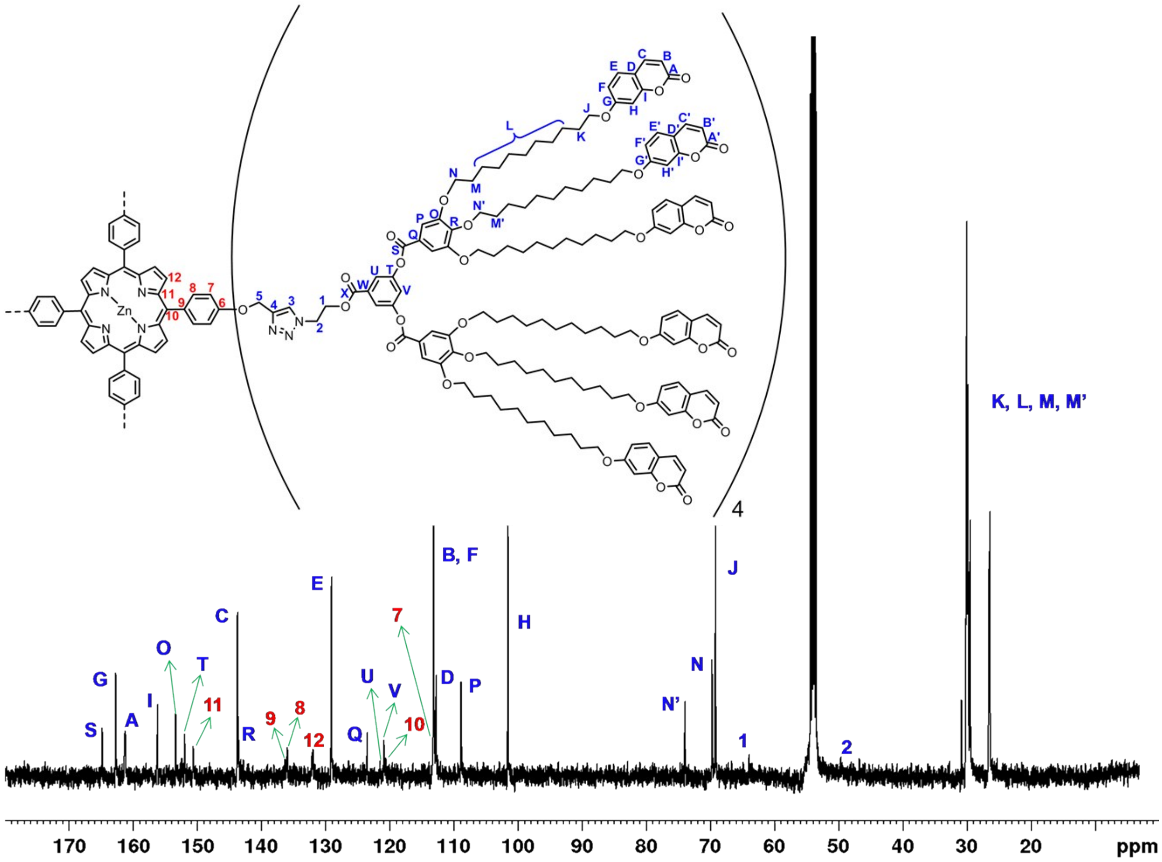


Figure S6. ^{13}C NMR spectrum (125 MHz, 298K, CD_2Cl_2) of **ZnP-d$_2$Cou**

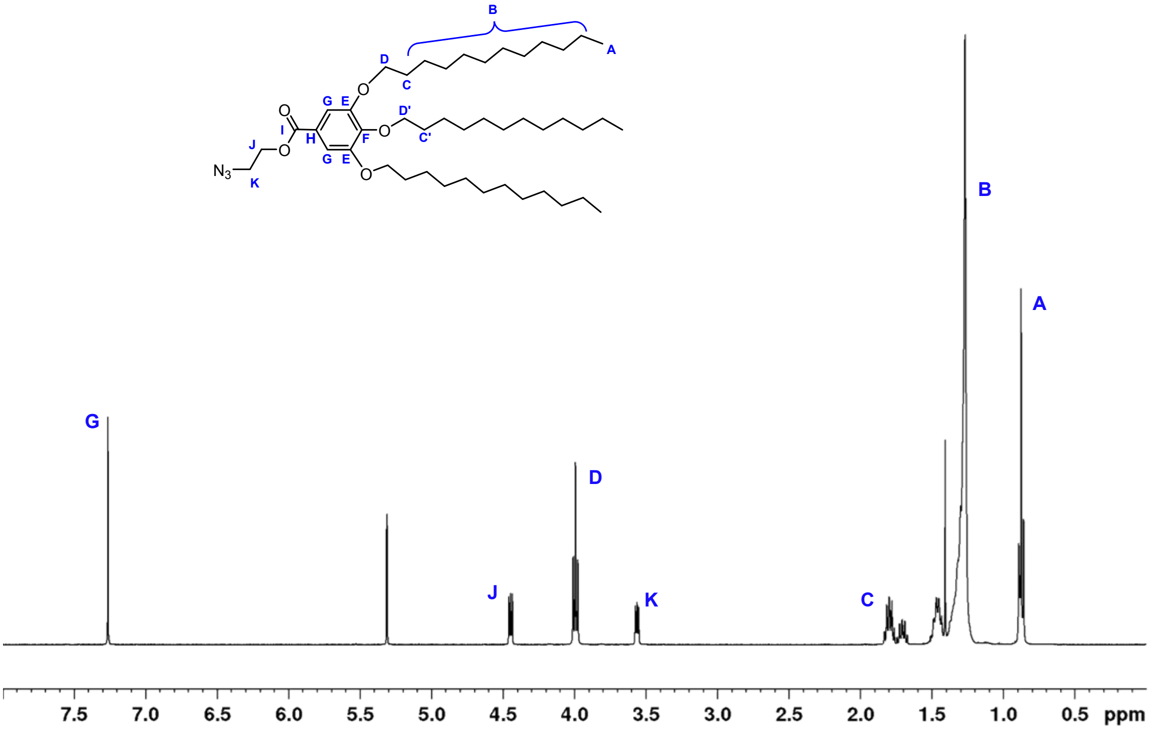


Figure S7 ^{1}H NMR spectrum (500 MHz, 298K, CD_2Cl_2) of **N_3-d_1C12**

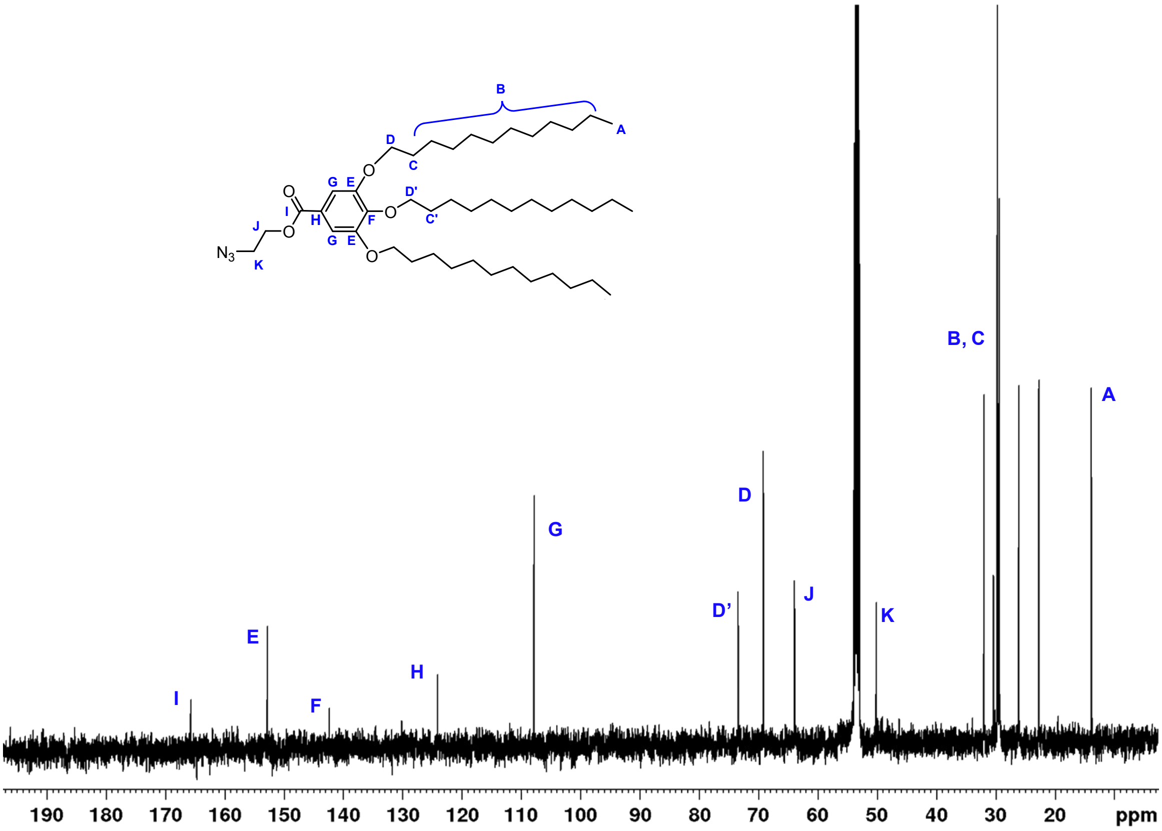


Figure S8. ^{13}C NMR spectrum (125 MHz, 298K, CD_2Cl_2) of **N_3-d_1C12**

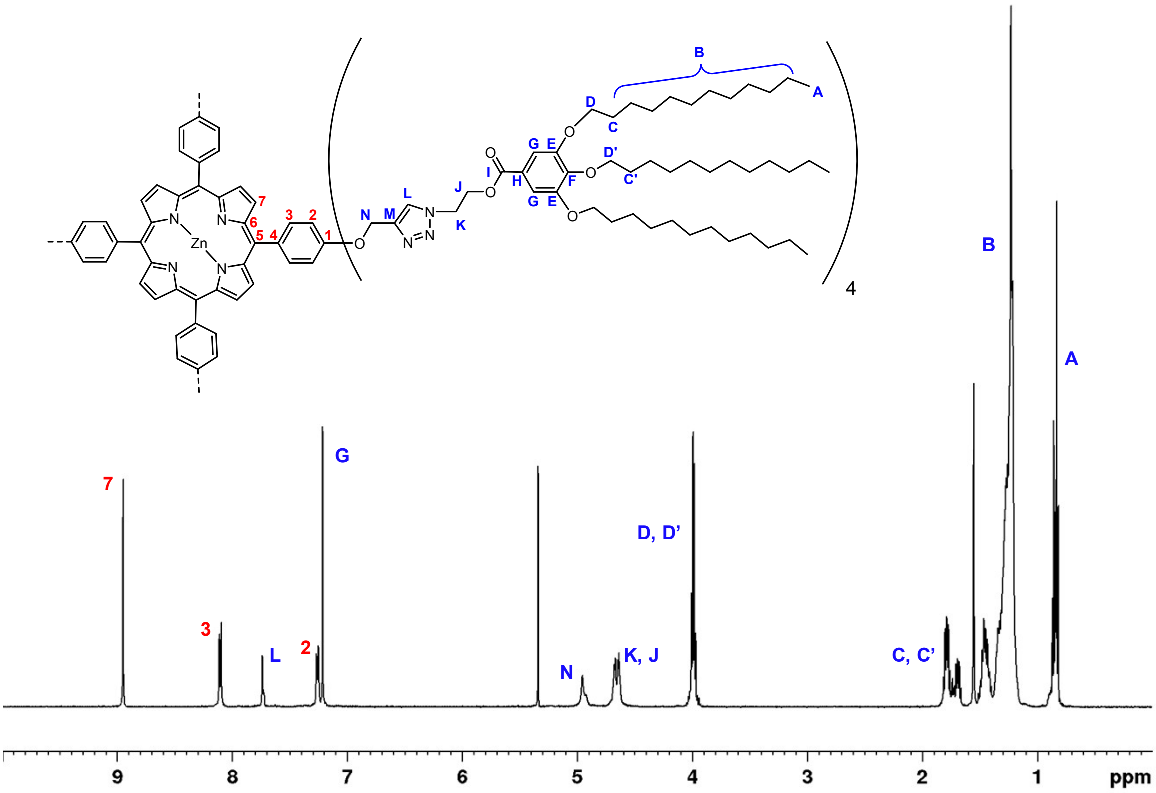


Figure S9. ^1H NMR spectrum (500 MHz, 298K, CD_2Cl_2) of **ZnP-d$_1$C12**

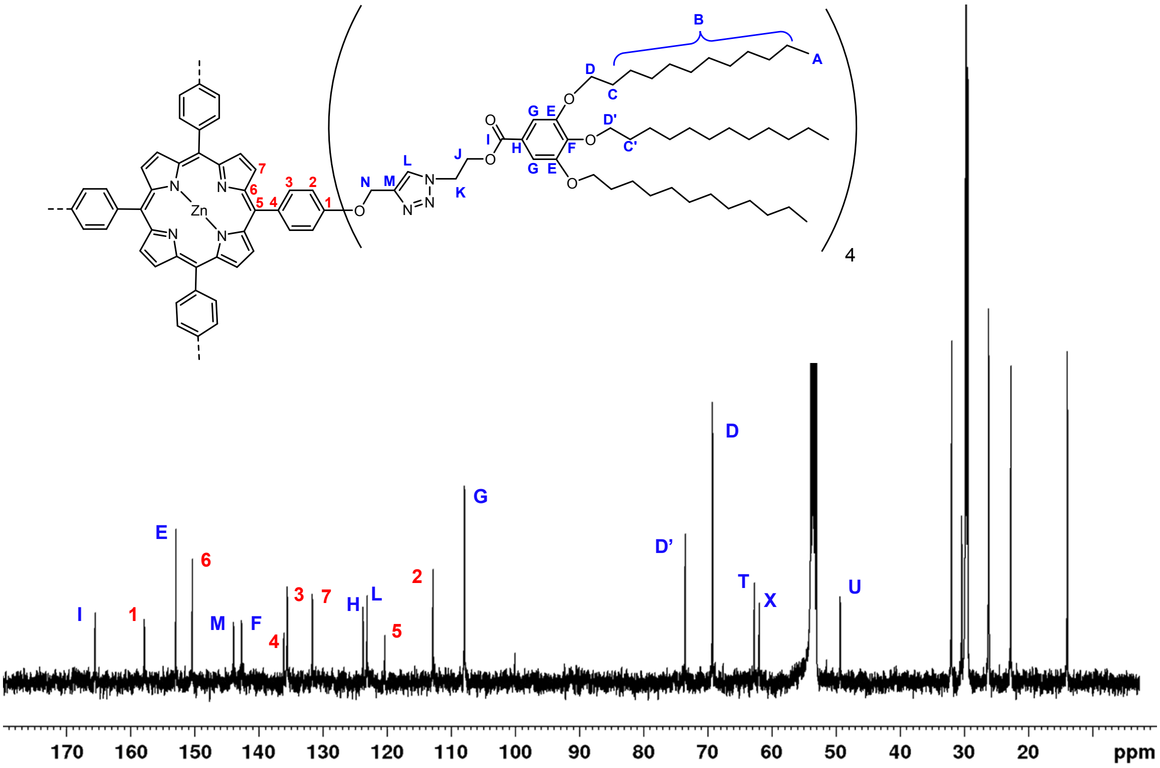


Figure S10. ^{13}C NMR spectrum (125 MHz, 298K, CD_2Cl_2) of **ZnP-d$_1$C12**

3.2. MALDI-TOF MS Spectra

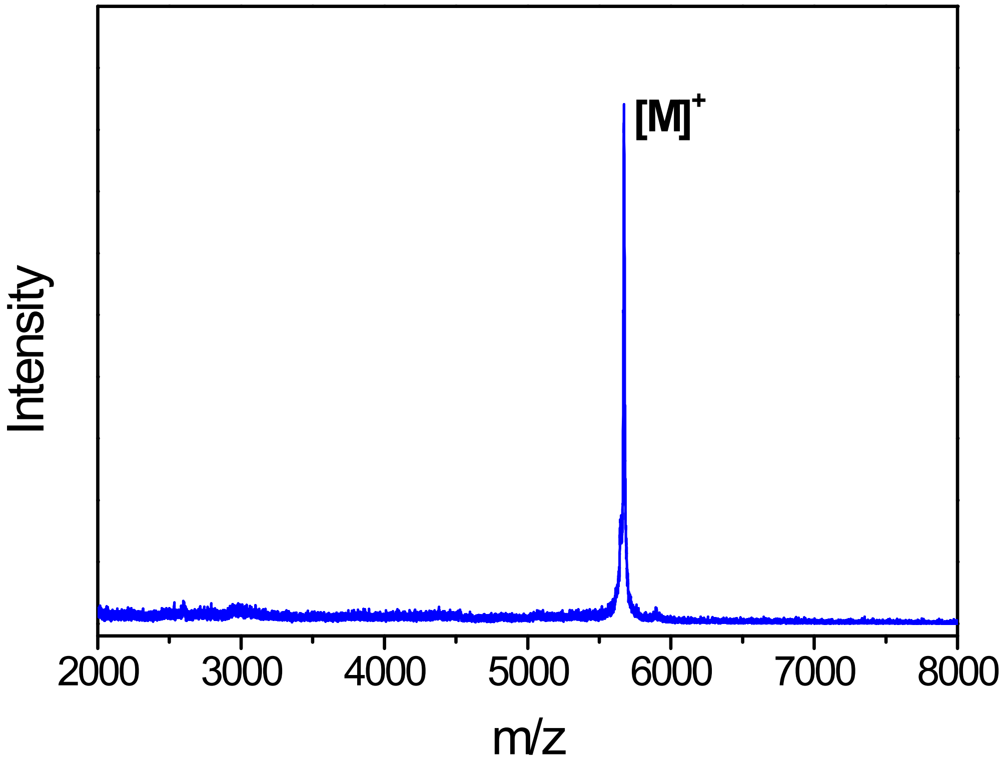


Figure S11. MALDI-TOF mass spectrum (MALDI$^+$, DCTB) of **ZnP-d$_1$Cou**.

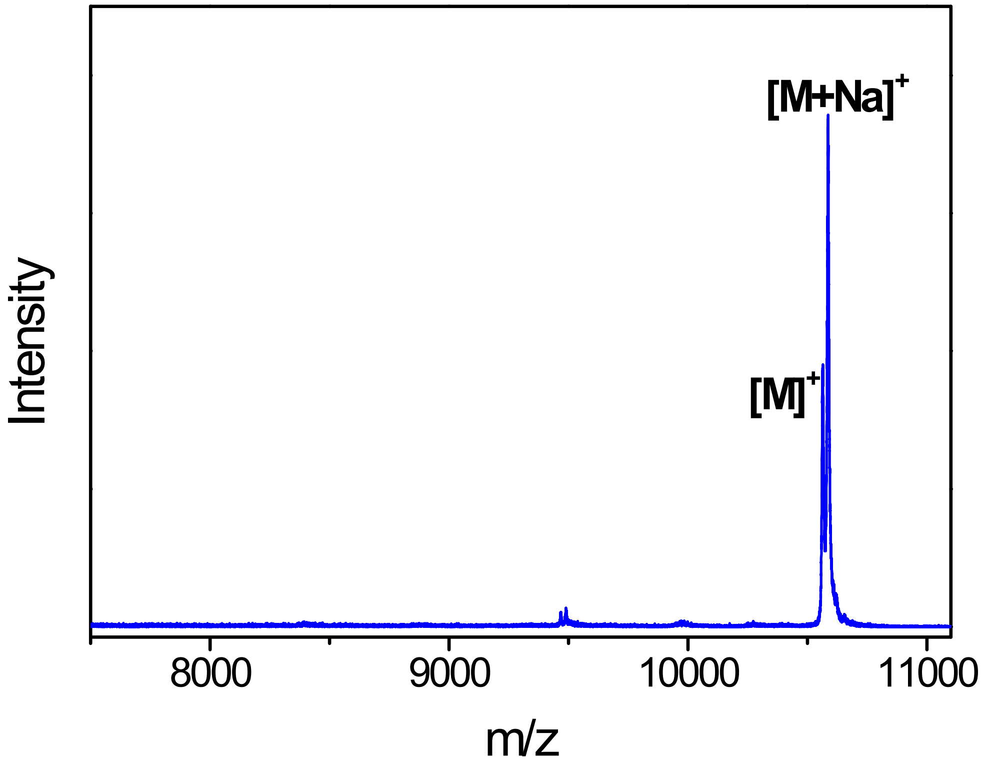


Figure S12. MALDI-TOF mass spectrum (MALDI$^+$, DCTB) of **ZnP-d$_2$Cou**.

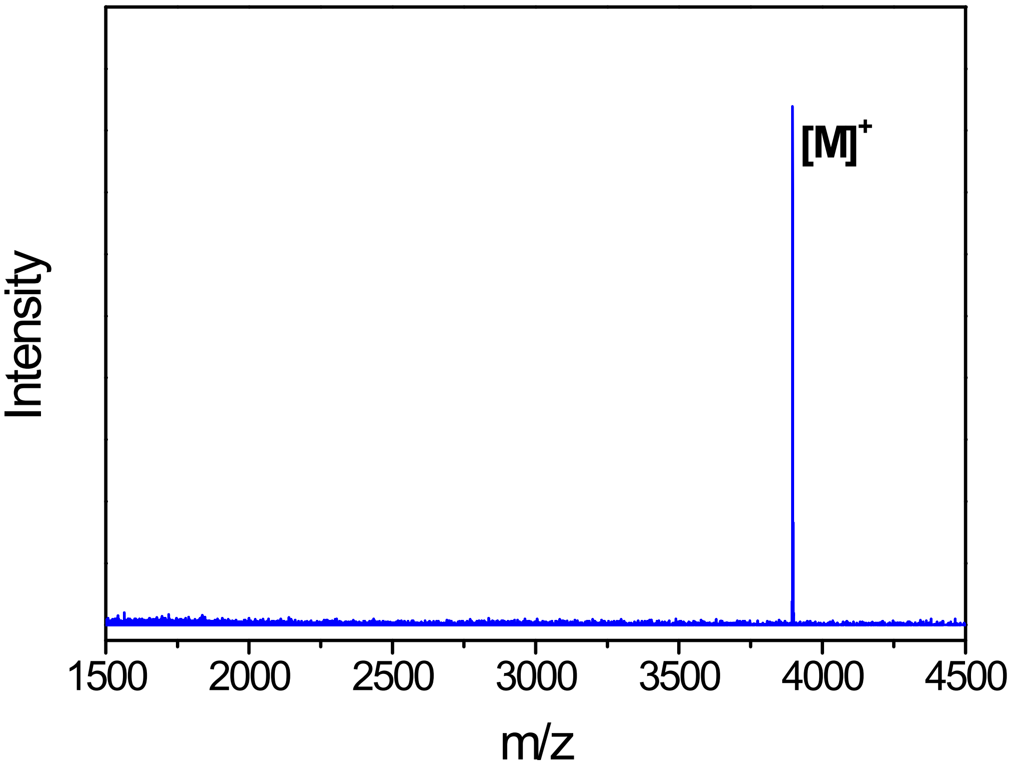


Figure S13. MALDI-TOF mass spectrum (MALDI$^+$, DCTB) of **ZnP-d$_1$C12**.

3.3. DSC curves

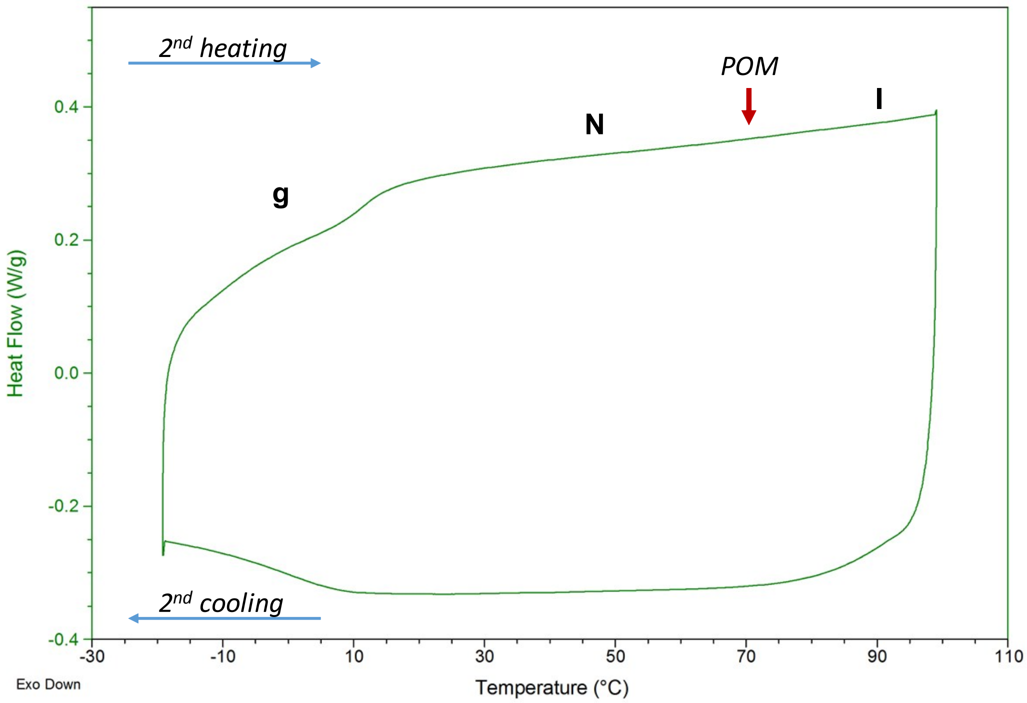


Figure S14. DSC traces of compound **N_3-d_2Cou** at a heating and cooling rate of 10 ºC min^{-1}; *g*: glass, N: nematic mesophase, I: isotropic liquid.

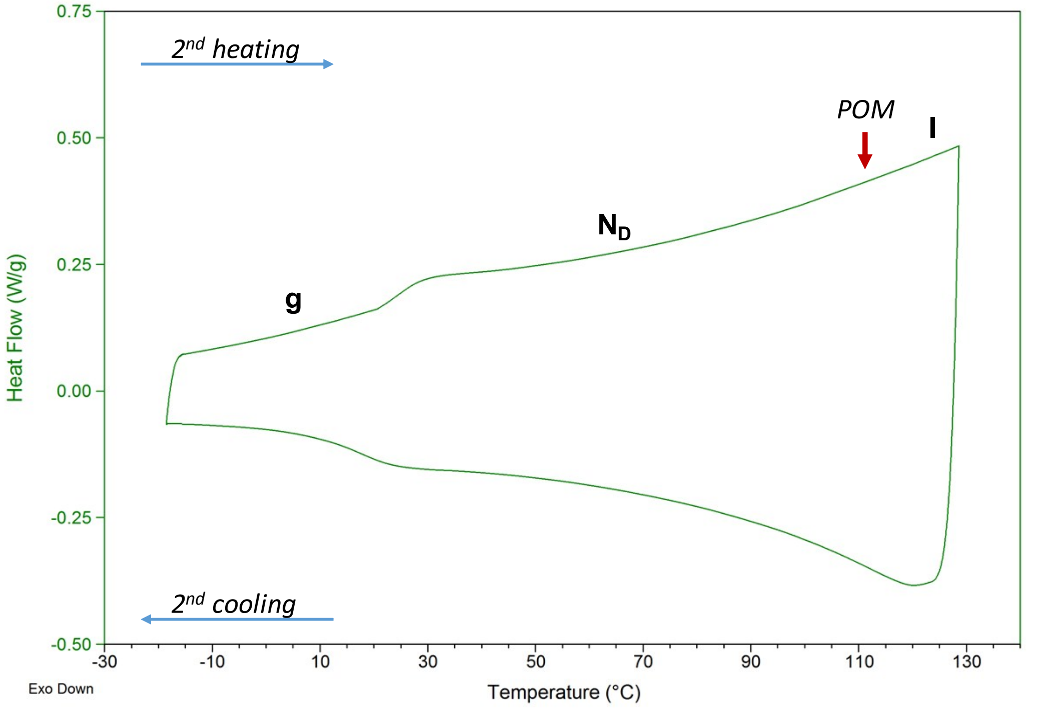


Figure S15. DSC traces of compound **ZnP-d_1Cou** at a heating and cooling rate of 10°C min^{-1}; *g*: glass, N_D: nematic discotic mesophase, I: isotropic liquid.

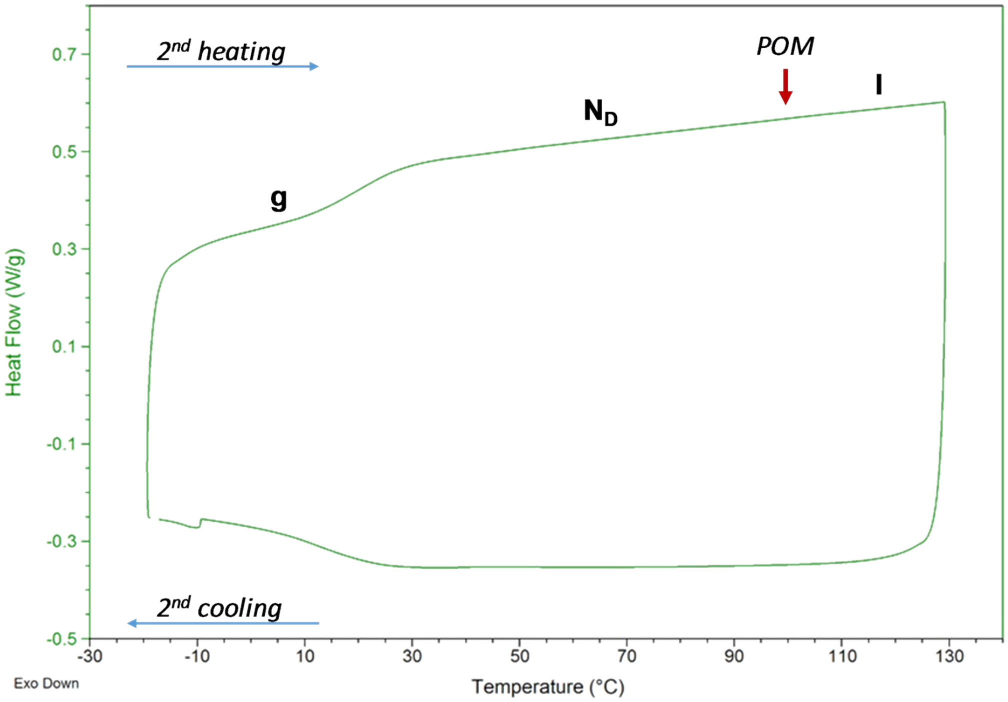


Figure S16. DSC traces of compound **ZnP-d$_2$Cou** at a heating and cooling rate of 10 °C min^{-1}; *g*: glass, N$_D$: nematic discotic mesophase, I: isotropic liquid.

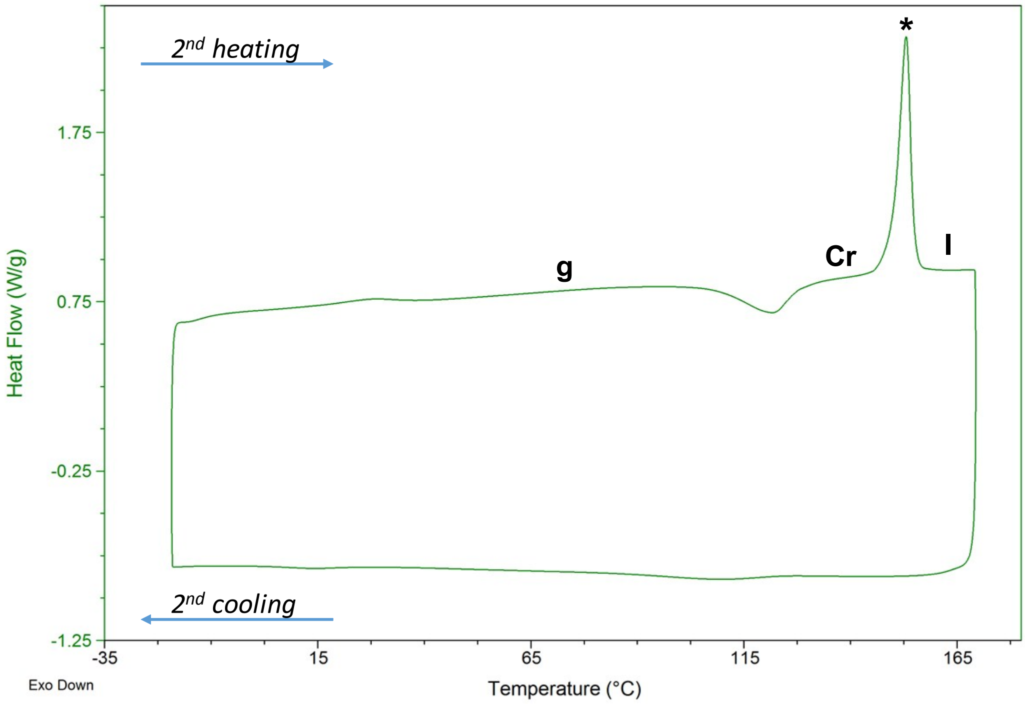


Figure S17. DSC traces of compound **ZnP-d$_1$C12** at a heating and cooling rate of 10 °C min^{-1}; *g*: glass, Cr: crystal, M: mesophase, I: isotropic liquid. (*Two transitions are detected by POM: Cr to M, and M to I)

3.4. XRD patterns

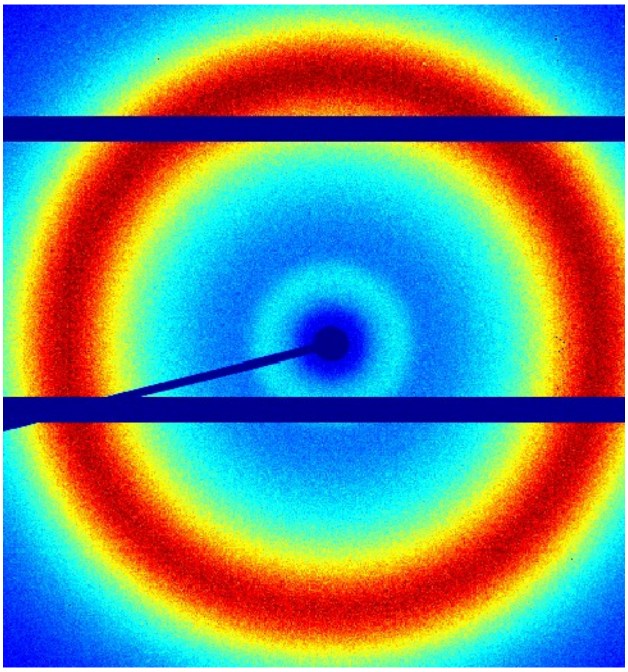


Figure S18. XRD pattern of compound **N_3-d_2Cou** at room temperature.

4. REFERENCES

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