Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Liquid Crystals from Shape-Persistent Porphyrin Stars with Intrinsic Free Space

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1) General Information – Materials and Equipment

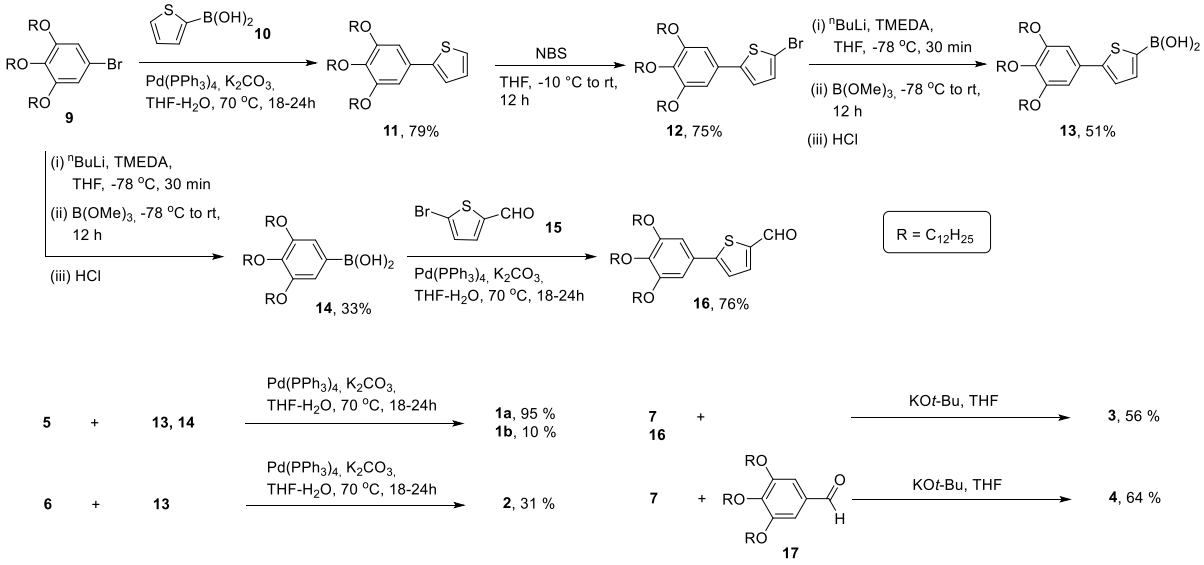
a) Materials

All commercial materials employed were used as received from Sigma Aldrich, abcr, and Acros Organics, without further purification, with the exceptions of pyrrole and $P(OEt)_3$, which were freshly distilled under reduced pressure. Solvents were distilled and dried via standard procedures. Silica gel (60-120 mesh) and (230-400 mesh) were used for chromatographic separation.

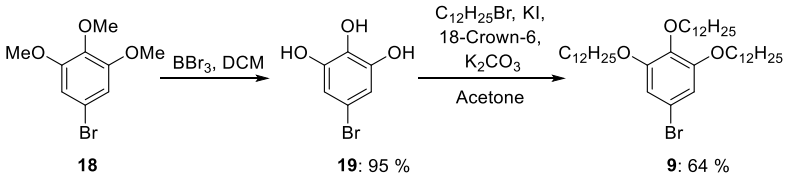
b) Equipment

Preparative recycling gel permeation chromatography was performed with the liquid chromatograph LC-20A (Shimadzu). The column set (PSS SDV 50 Å, 20·600 mm; PSS SDV 500 Å, 20·600 mm) was eluted with HPLC-grade $CHCl_3$ at a flow rate of 4.0 $mLmin^{-1}$. NMR spectra were recorded on a Bruker-Daltonics Avance-400 spectrometer operating at 400 MHz (^1H) or 100 MHz (^{13}C) with the residual protic solvent used as the internal standard. Mass spectra were recorded on a Bruker-Daltonics autflex II (MALDI). The studies of optical textures of the mesophases were realized with a Nikon Eclipse LV100Pol optical polarizing microscope equipped with a Linkam LTS420 heating stage and a Linkam T95-HS system controller. Thin film fluorescence spectra were recorded on a StellarNet BLACK-Comet CXR-100 spectrophotometer equipped with a Nikon Intensilight C-HGFI illuminator. UV-Vis- absorption studies in solution were performed with a PerkinElmer Lambda 35. Emission studies in solution were realized with a PTI QM-4/2003. The temperature dependent WAXS X-ray investigations were performed on a Bruker Nanostar (Detector Vantec2000, Microfocus copper anode X-ray tube Incoatec). The samples were prepared by fibre extrusion using a mini-extruder. The measurements were carried out in Mark capillaries (Hilgenberg) positioned perpendicular to the incident X-ray beam.

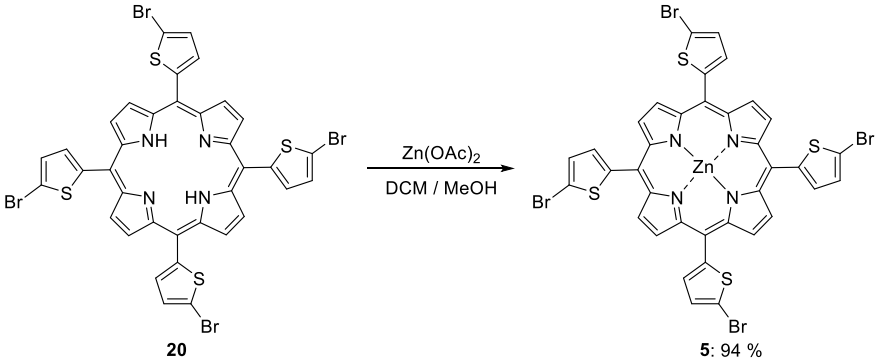
2) Synthesis



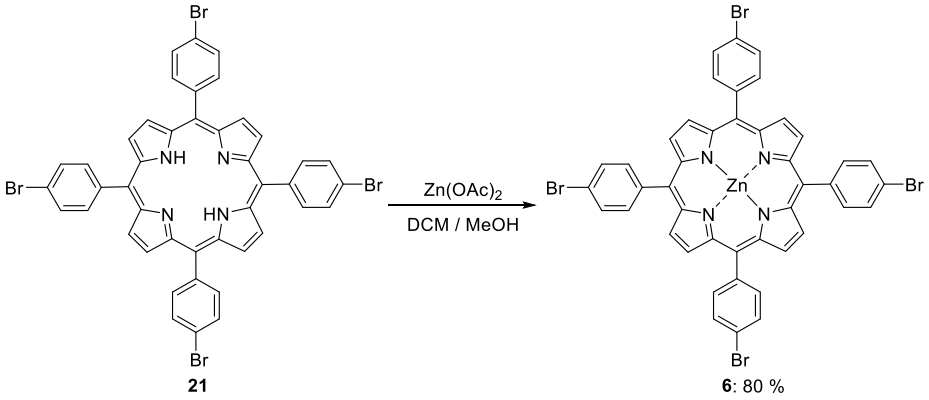
Scheme 1: Synthesis of the porphyrines **1**-**4**.



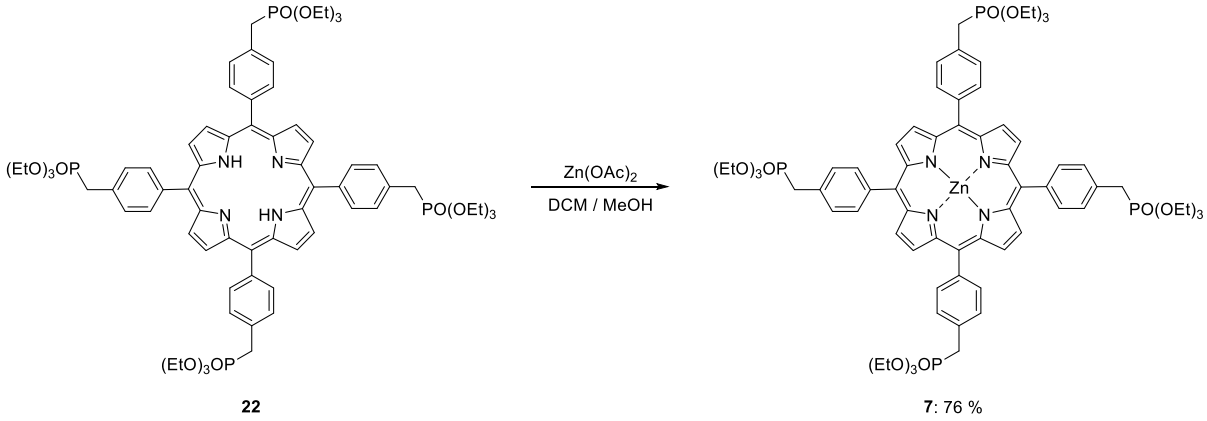
Scheme 2: Synthesis of the headgroup **9**.



Scheme 3: Synthesis of the core **5**.

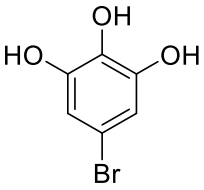


Scheme 4: Synthesis of the core **6**.



Scheme 5: Synthesis of the core **7**.

5-Bromobenzene-1,2,3-triol (**19**)



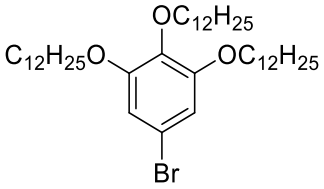
3.00 g (12.0 mmol) 5-Bromo-1,2,3-trimethoxybenzene (**18**) was dissolved in dry dichloromethane (DCM) under nitrogen atmosphere. At -78 °C, 3.76 mL (9.92 g, 40.0 mmol) BBr_3 was added and the resulting mixture was allowed to warm up to room temperature and was stirred for 24 hours. The reaction was completed by the addition of ice, the aqueous layer was extracted with ethyl acetate and the combined organic layers were dried over sodium

sulfate. The solvent was removed under reduced pressure to yield 2.73 g (11.9 mmol, 99 %) of a colorless solid.

^{1}H NMR (400 MHz, acetone-d_6): δ = 6.56 (bs, 2 H, Ar*H*), 7.52 (bs, 1 H, O*H*), 8.23 (bs, 2 H, O*H*) ppm.

The data is in agreement with the literature.[1]

5-Bromo-1,2,3-tris(dodecyloxy)benzene (**9**)



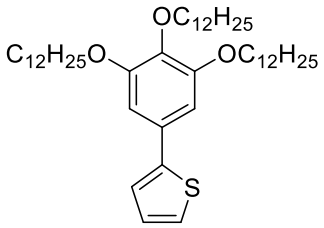
1.47 g (7.17 mmol) **19**, 13.5 g (97.6 mmol) K_2CO_3, 486 mg (2.93 mmol), KI and 181 mg (683 µmol) 18-Crown-6 were dissolved in acetone. After stirring for ten minutes, 10.1 mL (10.5 g, 42.0 mmol) dodecyl bromide was added and the mixture was heated up to 80 °C for 48 hours. After the reaction was complete, the solvent was removed enter reduced pressure and the residue was mixed with dest. water and ethyl acetate. The aqueous layer was extracted with ethyl acetate and the combined organic layers were dried over sodium sulfate. The solvent was subsequently removed under reduced pressure. The crude product was recrystallized from isopropanol to yield 3.26 g (4.59 mmol, 64 %) of a colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, ^3J = 6.84 Hz, 9 H, CH_2CH_3), 1.26-1.35 (m, 48 H, CH_2), 1.45 (qui, ^3J = 7.37 Hz, 6 H, $OCH_2CH_2CH_2$), 1.68-1.73 (m, 2 H, OCH_2CH_2), 1.78 (qui, ^3J = 6.91 Hz, 4 H, OCH_2CH_2), 3.91 (t, ^3J = 6.62 Hz, 2 H, OCH_2), 3.92 (t, ^3J = 6.50 Hz, 4 H, OCH_2), 6.67 (s, 2 H, ArH) ppm.

The data is in agreement with the literature.[1]

[1] T. Yasuda, T. Shimizu, F. Liu, G. Ungar, T. Kato *J. Am. Chem. Soc.* **2011**, 133, 34, 13437-13444.

2-(3,4,5-tris(dodecyloxy)phenyl)thiophene (**11**)

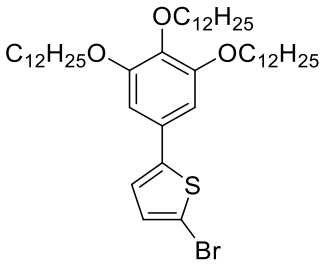


1.00 g (1.41 mmol) **9** and 189 mg (1.48 mmol) thiophene-2-boronic acid (**10**) were dissolved under nitrogen atmosphere in dry THF. After degassing for 20 minutes, 82.0 mg (71.0 µmol) Pd(dppf)Cl_2 and a solution of 292 mg (2.11 mmol) potassium carbonate in three ml dest. water were added and refluxed at 80 °C overnight. After the completed reaction, water was added and the mixture was extracted with DCM. The organic phases were combined, dried over sodium sulfate and the solvent was evaporated. The crude product was purified column chromatography (silica, cyclohexane : ethyl acetate = 20 : 1 (v/v)) to afford 956 mg (1.35 mmol, 96 %) of a colourless solid.

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 0.88 (t, ^3J = 6.9 Hz, 9 H, CH_3), 1.28-1.38 (m, 48 H, CH_2), 1.43-1.53 (m, 6 H, OCH$_2$CH$_2$CH_2), 1.72 (qui, ^3J = 7.1 Hz, 2 H, OCH$_2$CH_2), 1.81 (qui, ^3J = 7.0 Hz, 4 H, OCH$_2$CH_2), 3.93 (t, ^3J = 6.6 Hz, 2 H, OCH_2), 4.01 (t, ^3J = 6.5 Hz, 4 H, OCH_2), 6.78 (s, 2 H, ArH), 7.06 (dd, ^3J = 5.1 Hz; ^3J = 3.6 Hz, 1 H, ArH), 7.23 (dd, ^3J = 3.6 Hz; ^4J = 1.2 Hz, 1 H, ArH), 7.26 (dd, ^3J = 5.1 Hz; ^4J = 1.2 Hz, 1 H, ArH) ppm.

The data is in agreement with the literature.[1]

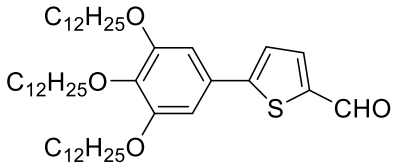
2-Bromo-5-(3,4,5-tris(dodecyloxy)phenyl)thiophene (**12**)



1.38 g (1.94 mmol) **11** and 345 mg (1.94 mmol) NBS were dissolved in dry THF at 0 °C. After stirring for 24 hours, the solvent was removed under reduced preassure and the crude product subjected to column chromatography (silica, cyclohexane : dichloromethane = 2 : 1 (v/v)) to afford 1.31 g (1.65 mmol, 85 %) of a colorless solid.

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 0.88 (t, ^3J = 6.9 Hz, 9 H, CH_3), 1.27-1.39 (m, 48 H, CH_2), 1.42-1.52 (m, 6 H, $OCH_2CH_2CH_2$), 1.71 (qui, ^3J = 7.1 Hz, 2 H, OCH_2CH_2), 1.81 (qui, ^3J = 7.0 Hz, 4 H, OCH_2CH_2), 3.93 (t, ^3J = 6.6 Hz, 2 H, OCH_2), 3.99 (t, ^3J = 6.4 Hz, 4 H, OCH_2), 6.69 (s, 2 H, ArH) 6.99 (d, ^3J = 3.9 Hz, 1 H, ArH), 7.03 (d, ^3J = 3.9 Hz, 1 H, ArH) ppm.

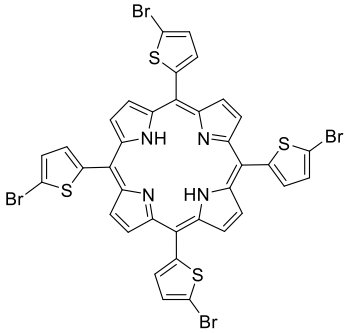
5-(3,4,5-Tris(dodecyloxy)phenyl)thienyl-2-carbaldehyde (**16**)



A nitrogen-degassed solution of THF (50 ml) and water (10 ml) was added to a mixture of K_2CO_3 (542 mg, 3.93 mmol), (3,4,5-tris(dodecyloxy)phenyl)boronic acid **14** (2.30 g, 3.41 mmol), 5-bromothiophene-2-carbaldehyde (500 mg, 3.41 mmol), and $Pd(PPh_3)_4$ (151 mg, 13.1 mmol) at room temperature. The resulting mixture was stirred at 70 ˚C for 16 hours under nitrogen atmosphere. The reaction mixture was then cooled, diluted with water, and then extracted three times with dichloromethane. The organic layer was washed with brine and dried over $MgSO_4$. After filtration and concentration in vacuum, the crude product was purified by column chromatography (silica, cyclohexane/dichloromethane = 1/1 (*v*/*v*)) to afford 1.06 g(1.43 mmol, 42 %) of a colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.88 (t, 9H, ^3J = 7.2 Hz), 1.26-1.38 (m, 48H), 1.45-1.52 (m, 6H), 1.74 (q, 2H, ^3J = 8.0 Hz), 1.83 (quint, 4 H, ^3J = 8.0 Hz), 3.98-4.04 (m, 6H), 6.84 (s, 2H), 7.30 (d, 1H, ^3J = 4.0 Hz), 7.71 (d, 1H, ^3J = 4.0 Hz), 9.87 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.1 (C_p), 22.7, 26.06, 26.08, 29.33, 29.35, 29.38, 29.57, 29.62, 29.65, 29.69, 29.71, 29.73, 29.74, 30.3, 31.91, 31.92, 69.3, 73.6 (C_s), 105.2, 123.6, 128.1 (C_t), 137.4, 139.6, 141.9, 153.5, 154.8 (C_q), 182.7 (CHO) ppm.

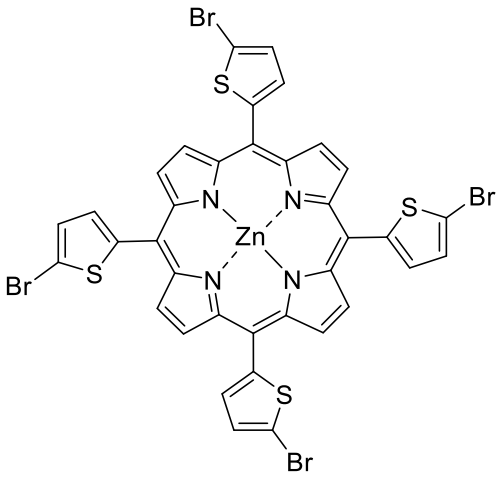
5,10,15,20-Tetrakis(5-bromothien-2-yl)porphyrin **20**



1.77 mL (15.0 mmol) 4-Bromothiophencarboxyaldehyde (**10**) and 1.05 mL pyrrole were dissolved in dichloromethane (DCM) under nitrogen atmosphere. After degassing for 20 minutes, 200 µL (2.76 mmol) $BF_3 \cdot Et_2O$ were added and the reaction was stirred at room temperature for 17 hours, followed by addition of 2.77 g (11.3 mmol) *p*-chloroanile was added and the reaction was stirred for six hours. After complete reaction, the solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica, cyclohexane) to yield 910 mg (6.95 mmol, 25 %) of a purple solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = -2.77 (s, 2 H, N*H*), 7.49 (d, ^3J = 3.7 Hz, 4 H, Ar*H),* 7.66 (d, ^3J = 3.6 Hz, 4 H, Ar*H),* 9.10 (s, 8 H, Ar*H*) ppm.

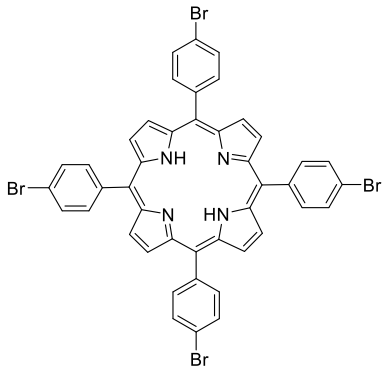
Zinc(II) 5,10,15,20-tetrakis(5-bromothien-2-yl)porphyrin (**5**)



350 mg (367 µmol) of porphyrin **20** and 121 mg (550 µmol) $Zn(OAc)_2 \cdot H_2O$ were dissolved in a mixture of 20 mL DCM and 5 mL MeOH. The reaction was stirred for five hours at room temperature. After complete reaction, saturated $NaHCO_3$-solution was added and the aqueous phase extracted with DCM. The combined organic layers were dried over Na_2SO_4 and the solvent removed under reduced pressure, to yield 350 mg (344 µmol, 94 %) of a purple solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, ^3J = 2.7 Hz, 4 H, Ar*H*), 7.66 (d, ^3J = 3.2 Hz, 4 H, Ar*H),* 9.22 (s, 8 H, Ar*H*) ppm.

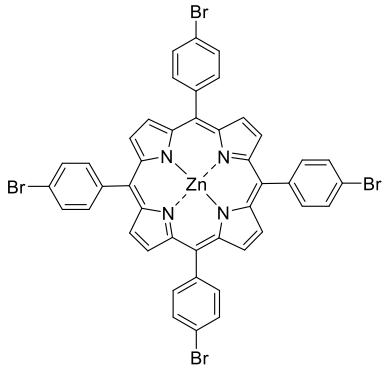
5,10,15,20-Tetrakis(4-bromophenyl)porphyrin (**21**)



1.54 g (8.29 mmol) 4-Bromobenzaldehyde (**10**) and 0.59 mL (8.51 mmol) pyrrole were dissolved in chloroform under nitrogen atmosphere. After addition of 329 mg (2.76 mmol) $BF_3 \cdot Et_2O$, the reaction was stirred at room temperature for one hour. 0.47 mL (343 mg, 3.39 mmol) NEt_3 and 1.52 g (6.18 mmol) TBTQ were added and the reaction was heated to 90 °C for one hour. After the completion of the reaction, the solvent was removed under reduced pressure and the crude product was isolated by column chromatography (silica, chloroform to afford 700 mg (1.43 mmol, 42 %) of a colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = -2.87 (s, 2 H, N*H*), 7.92 – 7.88 (AA'BB', 8 H, Ar*H*), 8.8 – 8.05 (AA'BB', 8 H, Ar*H*), 8.84 (s, 8 H, Ar*H*) ppm.

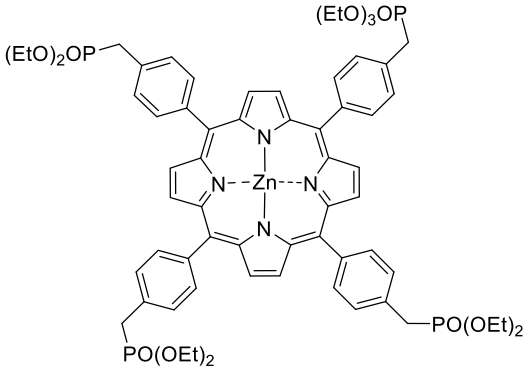
Zinc(II) 5,10,15,20-tetrakis(4-bromophenyl) porphyrin (**6**)



300 mg (322 µmol) of porphyrin **21** and 106 mg (484 µmol) $Zn(OAc)_2 \cdot H_2O$ were dissolved in a mixture of 20 mL DCM and 5 mL MeOH. The reaction was stirred for five hours at room temperature. Saturated $NaHCO_3$-solution was added and the aqueous phase extracted with

DCM. The combined organic layers were dried over Na_2SO_4 and the solvent removed under reduced pressure to yield 288 mg (289 µmol, 80 %) of a purple solid

Zinc(II) 5,10,15,20-Tetrakis-(α{*p*-[(diethoxyphosphoryl)methyl]phenyl})porphyrin (**7**)

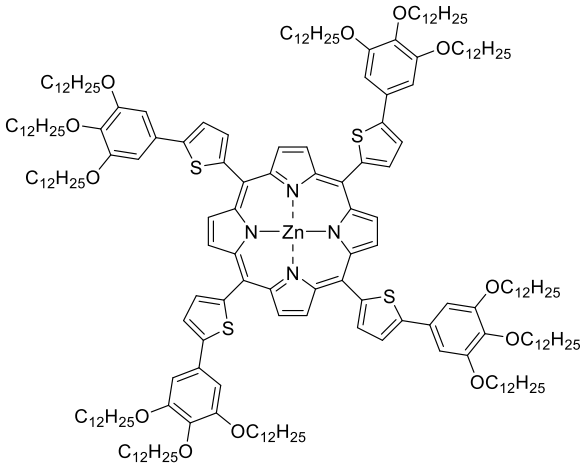


The precursor **22** was synthesized according to the literature[2]. 335 mg (276 µmol) of porphyrin **22** was diluted in 30 mL DCM and degassed for 30 min. 75.9 mg (414 µmol, 1.5 eq) ZnOAc were added and the mixture stirred at room temperature for 16 h. After completed reaction, the solvent was evaporated and the crude product was purified by column chromatography (Silica, DCM:EtOH 100:5) to afford 270 mg (211 µmol, 76%) of a purple solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.39 (t, ^3J = 7.08 Hz, 24 H, CH_3), 3.47 (d, $^2J_{HP}$ = 21.6 Hz, 8 H, CH_2), 4.24 – 4.15 (m, 16 H, CH_2), 8.11 (AA'BB', 8 H, Ar*H*), 8.16 – 7.62 (AA'BB', 8 H, Ar*H*), 8.84 (s, 8 H, Ar*H*) ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.6 (C_p), 33.1-34.5, 62.4 (C_s), 120.1 (C_q), 127.8 (C_t), 130.5 (C_q), 131.6, 134.7 (C_t), 142.2, 150.0 (C_q) ppm.

[2] Johann W. Buchler, Joachim R. Simon, *European Journal of Inorganic Chemistry* 2000, *2000*, 2615-2621.

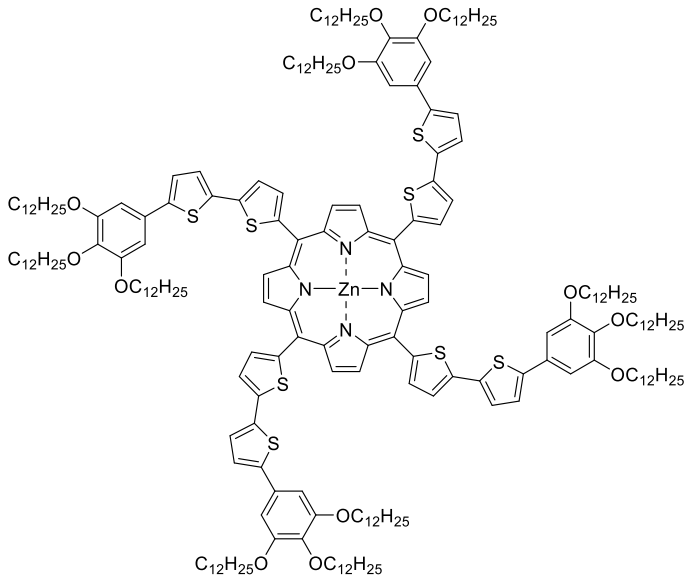
Zinc(II) 5,10,15,20-tetrakis(5-(3,4,5-tris(dodecyloxy)phenyl)thien-2-yl)porphyrin (**1a**)



50.0 mg (0.049 mmol, 1.0 eq.) core molecule **5**, 1.20 g (393 µmol, 8.0 eq.) boronic acid **14**, 17.0 mg (14.7 µmol, 0.3 eq.) tetrakis(triphenylphosphine)palladium(0) and 61.0 mg (0.441 mmol, 9.0 eq.) potassium carbonate were dissolved in 10 mL THF and 2 mL water. The mixture was refluxed at 80 °C overnight. The reaction mixture was diluted with 50 mL DCM and washed with 50 mL water. The aqueous phase was extracted twice with 50 mL DCM. The organic phases were combined, dried over magnesium sulfate and the solvent was evaporated. The crude product was purified by GPC (chloroform) to afford 150 mg (0.047 mmol, 95%) of the solid product **1a** (mp. 74 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92-0.86 (m, 42H), 1.54-1.49 (m, 26H), 1.39-1.26 (m, 220H), 1.91-1.77 (m, 26H), 4.13-4.01 (m, 24H), 7.07 (s, 8H), 7.64 (d, ^{3}J = 4.1 Hz, 4H), 7.85 (d, ^{3}J = 4.1 Hz, 4H), 9.30 (s, 8H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 14.1 (C_p), 22.7, 22.7, 26.2, 29.3, 29.4, 29.6, 29.7, 29.7, 29.8, 29.8, 30.4, 31.9, 32.0, 69.3, 73.6 (C_s), 104.8 (C_t), 113.1, 121.8 (C_q), 129.4, 132.1, 134.4 (C_t), 138.4, 142.5, 146.9, 151.2, 153.6 (C_q) ppm; MALDI-HRMS, m/z: calcd: 3214.3035 [$M^{+\cdot}$], found: 3214.3085 [$M^{+\cdot}$].

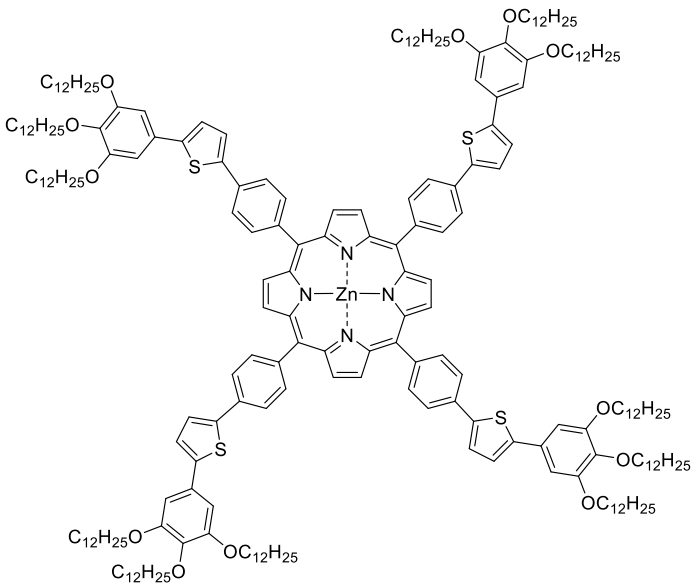
Zinc(II) 5,10,15,20-tetrakis(5'-(3,4,5-tris(dodecyloxy)phenyl)-[2,2'-bithiophen]-5-yl)porphyrin (**1b**)



50.0 mg (0.049 mmol) core molecule **5**, 298 mg (0.393 mmol) boronic acid **13**, 17.0 mg (0.0147 mmol) tetrakis(triphenylphosphine)palladium(0) and 61.0 mg (0.441 mmol) potassium carbonate were dissolved under nitrogen atmosphere in 6 mL THF and 2 mL water. The mixture was degassed and refluxed at 80 °C overnight. After completed reaction, water was added and the mixture was extracted with dichloromethane. The organic phases were combined, dried over sodium sulfate and the solvent was evaporated. The crude product was purified by GPC (chloroform) to afford 10 mg (0.0047 mmol, 10 %) of a green waxy solid **1b** (melting interval 130-189 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91-0.86 (m, 36 H), 1.37-1.27 (m, 192 H), 1.54-1.49 (m , 24 H), 1.88-1.73 (m, 24 H), 4.00 (t, ^{3}J = 6.6 Hz, 8 H), 4.06 (t, ^{3}J = 6.4 Hz, 16 H), 6.84 (s, 8 H), 7.36 (d, ^{3}J = 3.7 Hz, 4 H), 7.36 (d, ^{3}J = 3.8 Hz, 4 H), 7.61 (d, ^{3}J = 3.6 Hz, 4 H), 7.82 (d, ^{3}J = 3.6 Hz, 4 H), 9.32 (s, 8 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.3 (C_p) 14.3 (C_p), 22.8, 22.9, 26.3, 29.5, 29.6, 29.8, 29.9, 30.5, 32.1, 69.4, 73.8, 77.4 (C_s), 104.8 (C_t), 113.1, 122.8 (C_q), 123.7, 124.8 (C_t), 129.4, 132.4, 134.5 (C_t), 136.2, 138.4, 140.1, 142.2, 144.0, 151.4, 153.6 (C_q) ppm; MALDI-HRMS, m/z: calcd: 3542.2543 [$M^{+\bullet}$], found: 3542.2607 [$M^{+\bullet}$].

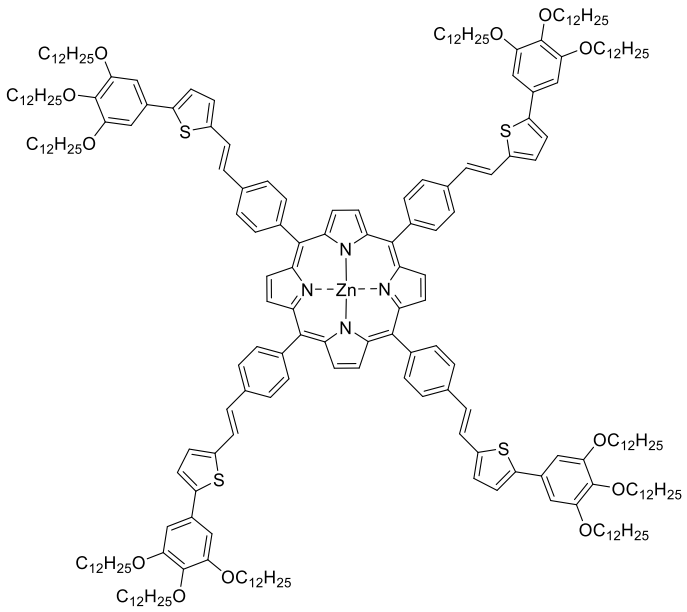
Zinc(II) 5,10,15,20-tetrakis(4-(5-(3,4,5-tris(dodecyloxy)phenyl)thiophen-2-yl)phenyl)porphyrin (**2**)



40.0 mg (0.040 mmol, 1.0 eq.) core molecule **6**, 622 mg (0.822 mmol, 20.4 eq.) boronic acid **13**, 9.0 mg (0.012 mmol, 0.3 eq.) Pd(dppf)Cl_2 and 55.3 mg (0.402 mmol, 10.0 eq.) potassium carbonate were dissolved under nitrogen atmosphere in 6 mL THF and 2 mL water. The mixture was degassed and refluxed at 80 °C overnight. Water was added and the mixture was extracted with dichloromethane. The organic phases were combined, dried over sodium sulfate and the solvent was evaporated. The crude product was purified by GPC (chloroform) to afford 44 mg (0.0124 mmol, 31%) of a green solid **2** (clearing point 161 °C).

^{1}H NMR (400 MHz, CD_2Cl_2) δ = 0.77-0.83 (m, 36 H), 1.21-1.33 (m, 192 H), 1.40-1.49 (m, 24 H), 1.64-1.71 (m, 8 H), 1.75-1.82 (m, 16 H), 3.90 (t, ^3J = 6.6 Hz, 8 H), 4.00 (t, ^3J = 6.4 Hz, 16 H), 6.85 (s, 2 H, Ar*H*), 7.30 (d, ^3J = 3.8 Hz, 4 H, Ar*H*), 7.54 (d, ^3J = 3.8 Hz, 4 H, Ar*H*), 7.96-7.98 (AA'BB', 8 H, Ar*H*), 8.18-8.20 (AA'BB', 8 H, Ar*H*), 9.00 (s, 8 H, Ar*H*) ppm; ^{13}C NMR (100 MHz, CD_2Cl_2) δ = 14.3 (C_p), 22.9, 22.9, 26.3, 29.5, 29.6, 29.6, 29.8, 29.9, 29.9, 29.9, 30.5, 32.1, 32.1, 69.4, 73.8, 76.8, 77.2, 77.4, 77.5 (C_s), 104.8 (C_t), 120.9 (C_q), 123.8, 124.1, 124.5 (C_t), 129.7(C_q), 132.2 (C_t), 133.7 (C_q), 135.2(C_t), 138.4, 142.0, 142.9, 144.6, 150.3, 153.6 (C_q) ppm; MALDI-HRMS, m/z: calcd: 3518.4287 [$M^{+\cdot}$], found: 3518.4274 [$M^{+\cdot}$].

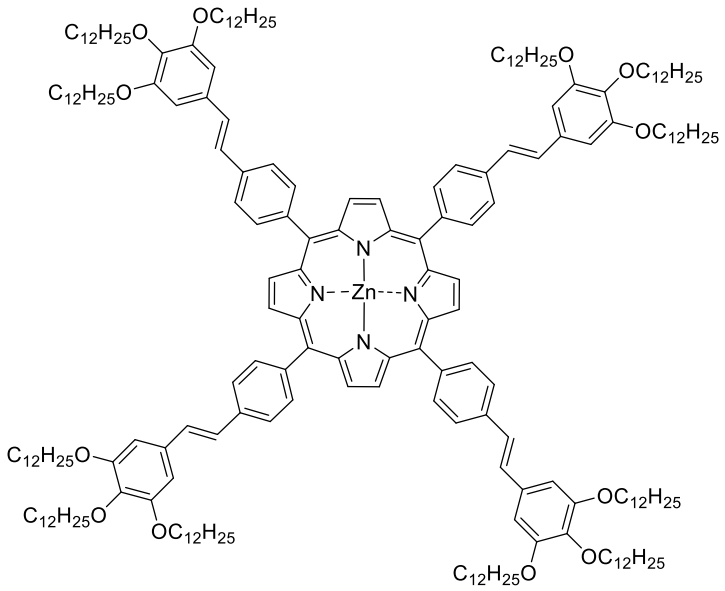
Zinc(II) 5,10,15,20-tetrakis(4-((E)-2-(5-(3,4,5-tris(dodecyloxy)phenyl)thiophen-2-yl)vinyl)-phenyl)porphyrin **3**



60 mg (46.9 µmol) core molecule **7** and 174 mg (235 µmol, 5 eq.) arm molecule **16** were dissolved under nitrogen atmosphere in 20 mL dry THF. 18.8 mg (469 µmol, 10 eq.) NaH (60 % in mineral solution) were added and the mixture stirred at room temperature for two days. After completed reaction, the solution was quenched at 0 °C with MeOH and the solvent was evaporated. The crude product was diluted in a small amount of DCM, poured into cold methanol and stored at 4 °C over night. The precipitated solid was filtered and purified by GPC (chloroform) to afford 95.2 mg (26.2 µmol, 56 %) of a green solid **3** (mp. 147 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92 – 0.86 (m, 36 H, CH_3), 1.43 – 1.20 (m, 96 H, CH_2), 1.81 – 1.74 (m, 8 H, OCH_2CH_2), 1.56 – 1.46 (m, 24 H, $OCH_2CH_2CH_2$), 1.90 – 1.81 (m, 16 H, OCH_2CH_2), 4.01 (t, ^{3}J = 6.60 Hz, 8 H, OCH_2), 4.08 (t, ^{3}J = 6.48 Hz, 16 Hz, OCH_2), 6.85 (s, 8 H, Ar*H*), 7.12 (d, ^{2}J = 3.90 Hz, 4 H, Ar*H*), 7.18 (d, ^{2}J = 4.08 Hz, 4 H, Ar*H*), 7.25 (d, ^{3}J = 15.9 Hz, 4 H, C*H*) 7.51 (d, ^{3}J = 16.1 Hz, 4 H, C*H*), 7.86 (AA'BB', 8 H, Ar*H*'), 8.18 (AA'BB', 8 H, Ar*H*), 9.00 (s, 8 H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.3 (C_p), 26.3, 26.3, 30.5, 22.9 – 32.1, 69.4, 73.8 (C_s), 104.8 (C_t), 121.1 (C_q), 122.8, 123.5, 124.7, 127.8, 127.9, 129.6 (C_t), 132.1 (C_q), 135.1 (C_t), 136.4, 138.5, 142.1, 143.9, 150.2, 153.6 (C_q) ppm; MALDI-HRMS, m/z: calcd: 3622.4913 ([$M^{+\cdot}$]), found: 3622.5073 ([$M^{+\cdot}$]).

Zinc(II) 5,10,15,20-tetrakis(4-((*E*)-3,4,5-tris(dodecyloxy)phenylethenyl)phenyl)porphyrin **4**



70 mg (55.0 µmol) core molecule **7** and 181 mg (275 µmol, 5 eq.) arm molecule **17** were dissolved under nitrogen atmosphere in 20 mL dry THF. Afterwards, 20.8 mg (550 µmol, 10 eq.) NaH (60 % in mineral solution) and 0.5 ml Pyridine were added and stirred at room temperature for four days. After completed reaction, the solution was quenched at 0 °C with MeOH and the solvent was evaporated. The crude product was diluted in a small amount of DCM, poured into cold methanol and stored at 4 °C overnight. The precipitated solid was filtered and purified by GPC (chloroform) to afford 117 mg (35.5 µmol, 64 %) of a green solid **4** (mp. 139 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.93 – 0.85 (m, 36 H, C*H*$_3$), 1.45 – 1.24 (m, 96 H, C*H*$_2$), 1.58 – 1.48 (m, 24 H, OCH$_2$CH$_2$C*H*$_2$), 1.84 – 1.76 (m, 8 H, OCH$_2$C*H*$_2$), 1.92 – 1.84 (m, 16 H, OCH$_2$C*H*$_2$), 4.03 (t, ^{3}J = 6.60 Hz, 8 H, OC*H*$_2$), 4.11 (t, ^{3}J = 6.48 Hz, 16 H, OC*H*$_2$), 7.31 (d, ^{3}J = 16.5 Hz, 4 H, Ar*H*), 7.35 (d, ^{3}J = 16.5 Hz, 4 H, Ar*H*), 7.90 (AA'BB', 8 H, Ar*H*), 8.23 (AA'BB', 8 H, Ar*H*), 9.04 (s, 8 H, Ar*H*) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.3 (C_p), 26.3, 32.1 – 29.9, 29.6, 30.6, 69.5, 73.7 (C_s), 105.5 (C_t), 121.1 (C_q), 124.8, 129.8, 132.2 (C_t), 132.8 (C_q), 135.1 (C_t), 136.7, 138.5, 142.1, 150.3, 153.4 (C_q) ppm; MALDI-HRMS, m/z : calcd: 3294.5404 ([$M^{+\cdot}$]), 3294.5552 ([$M^{+\cdot}$]).

3) Density measurement

Five solutions were prepared from water and sodium chloride solution, in which a thread of the substance floated in the middle. The mass of the empty (m_1), the water-filled (m_2) and the solution-filled (m_3) pycnometer was determined. Using

$$\rho_S = \frac{m_3 - m_1}{m_2 - m_1} \cdot \rho_W$$

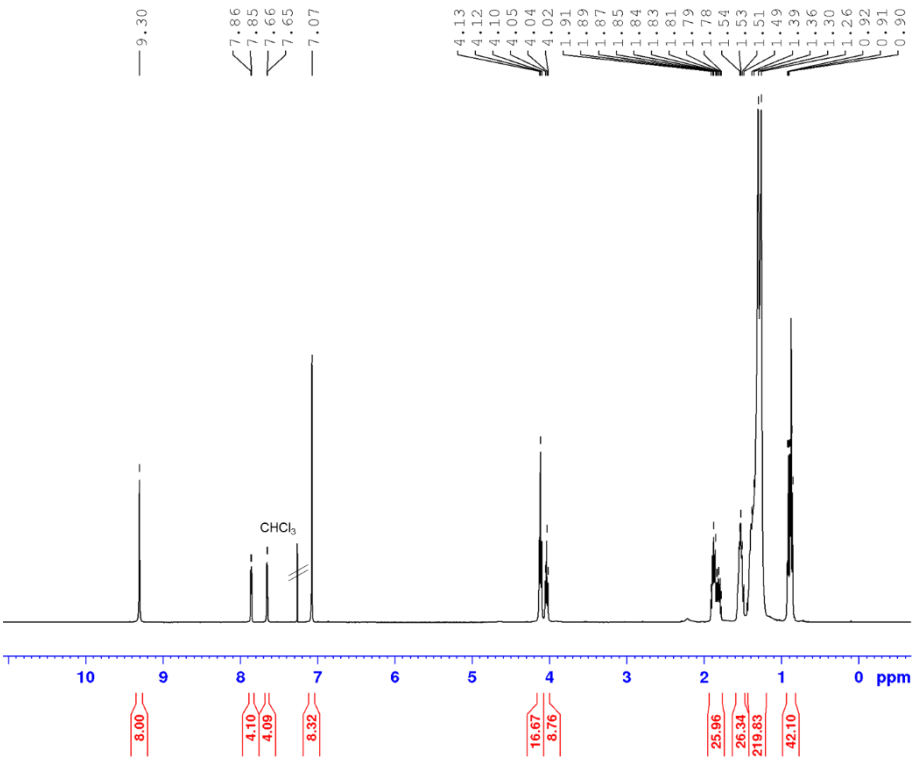
with ρ_S = density of the prepared solution and ρ_W = density of water at 296 K,[3] the density of the prepared solution was determined. An average value of the five determined densities was calculated and assumed as the density for the thread used.

N°	ρ(**4**) [g/cm^{-1}]	ρ(**3**) [g/cm^{-1}]
1	1.034	1.024
2	1.037	1.025
3	1.039	1.018
4	1.032	1.032
5	1.033	1.033
Average	1.035	1.026

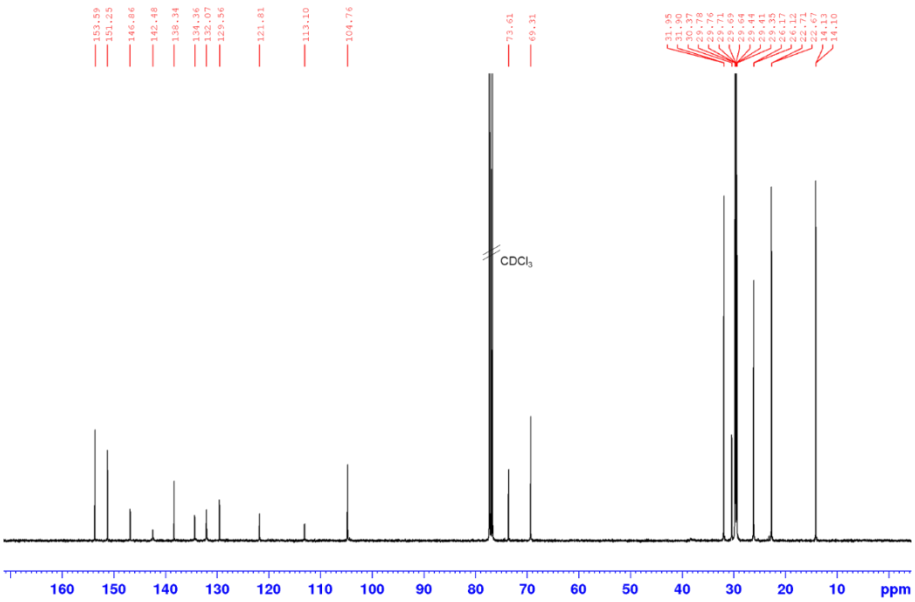
[3] W. Wagner, A. Pruß, *J. Phys. Chem. Ref. Data* **2002**, *31*, 387 – 535

4) NMR Spectra

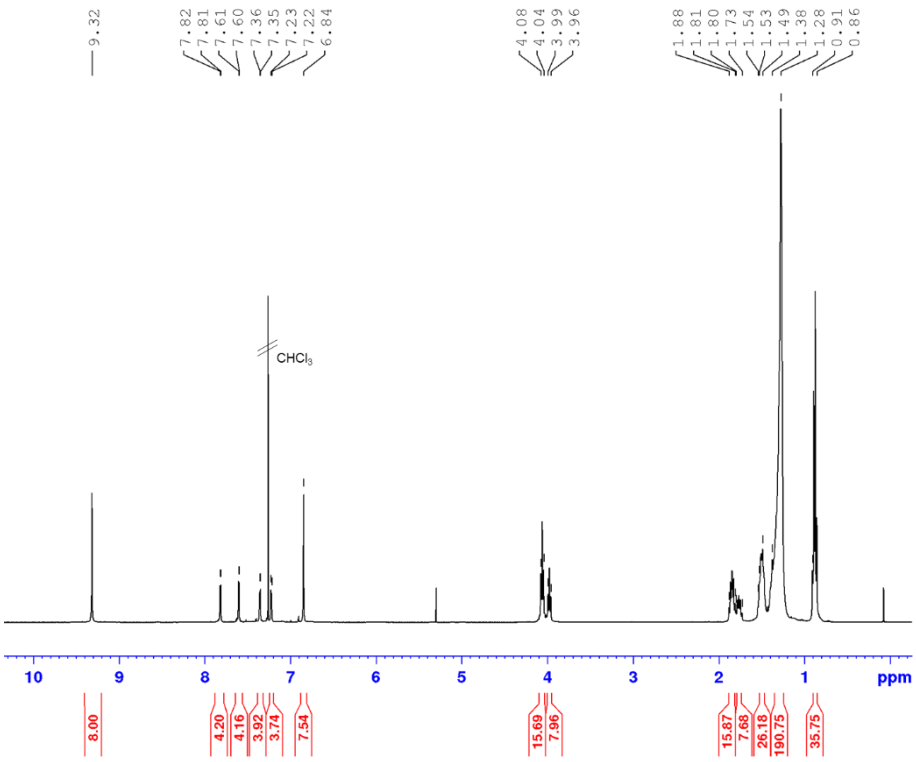
^{1}H NMR (400 MHz) spectrum of **1a** in $CDCl_3$



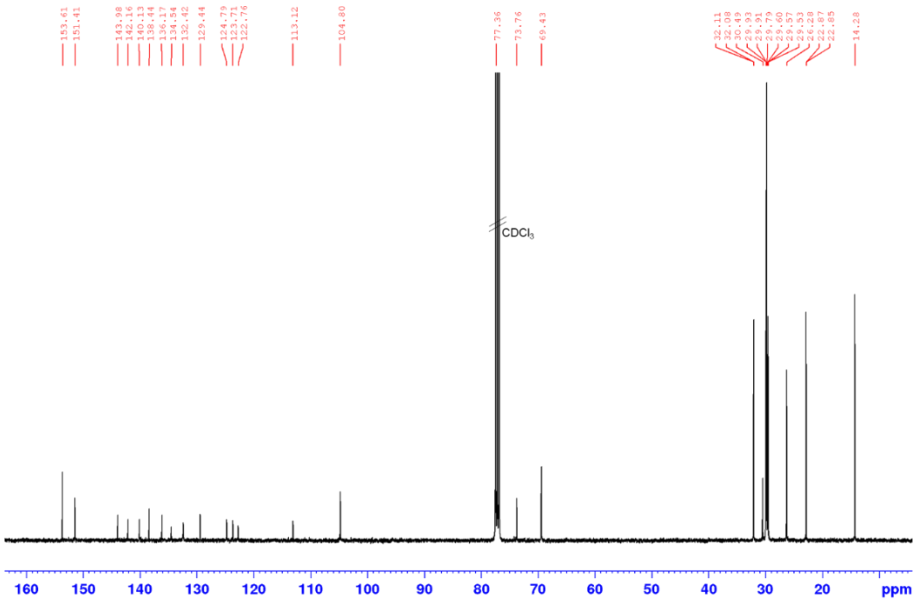
^{13}C NMR (100 MHz) spectrum of **1a** in $CDCl_3$



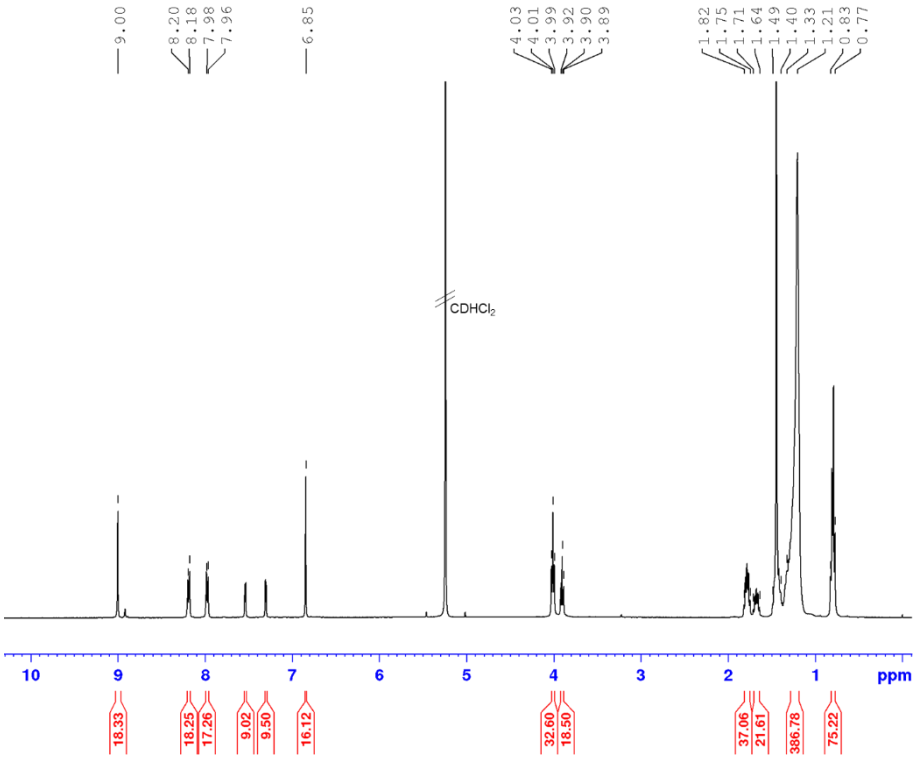
^{1}H NMR (400 MHz) spectrum of **1b** in $CDCl_3$



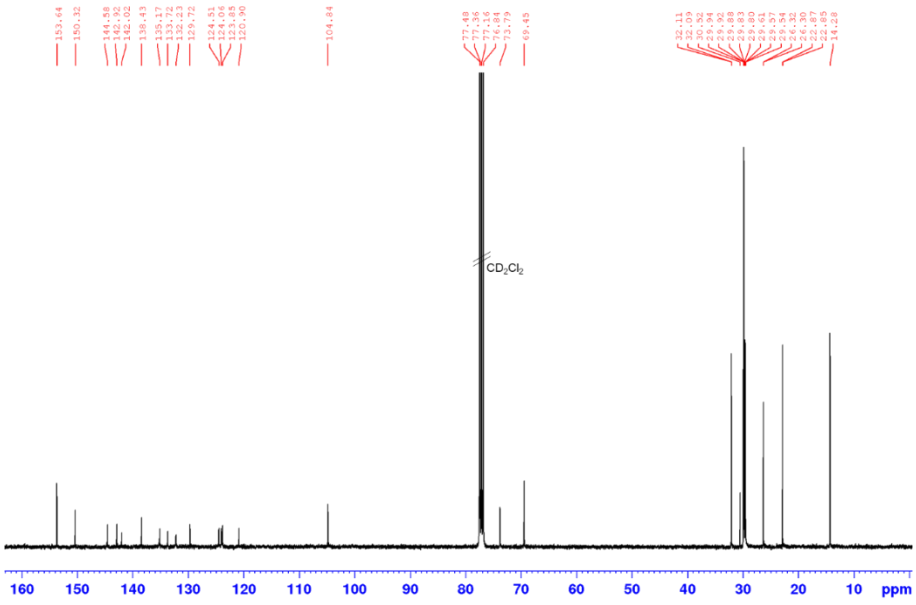
^{13}C NMR (100 MHz) spectrum of **1b** in $CDCl_3$



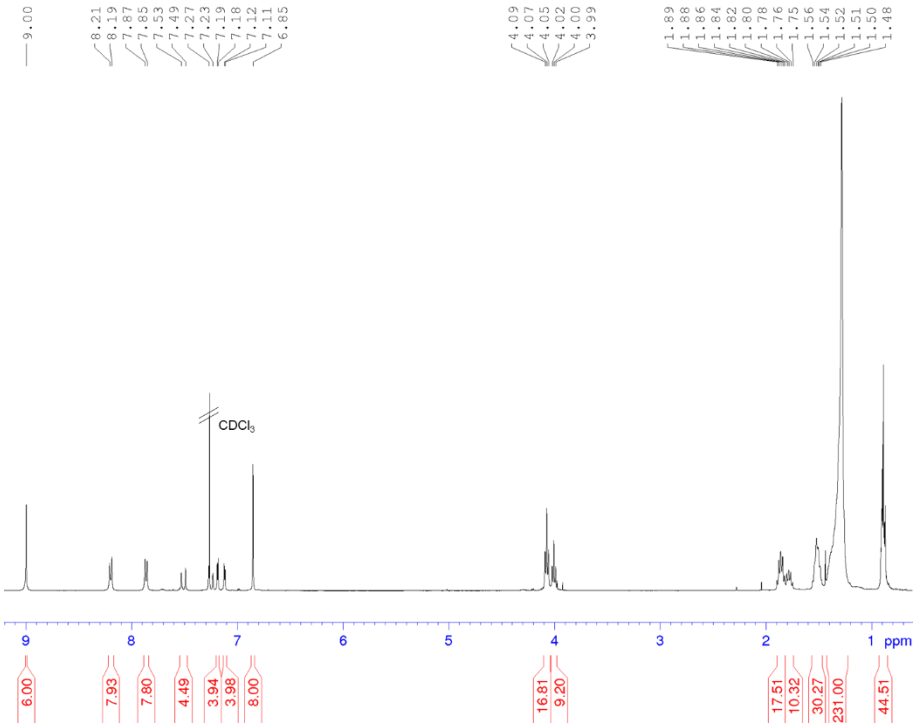
^{1}H NMR (400 MHz) spectrum of **2** in CD_2Cl_2



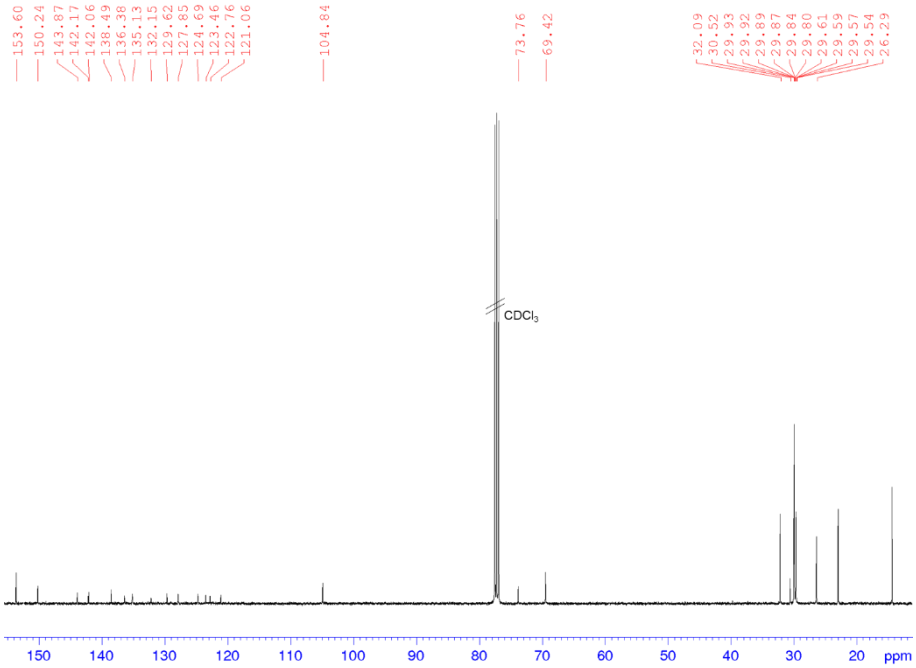
^{13}C NMR (100 MHz) spectrum of **2** in CD_2Cl_2



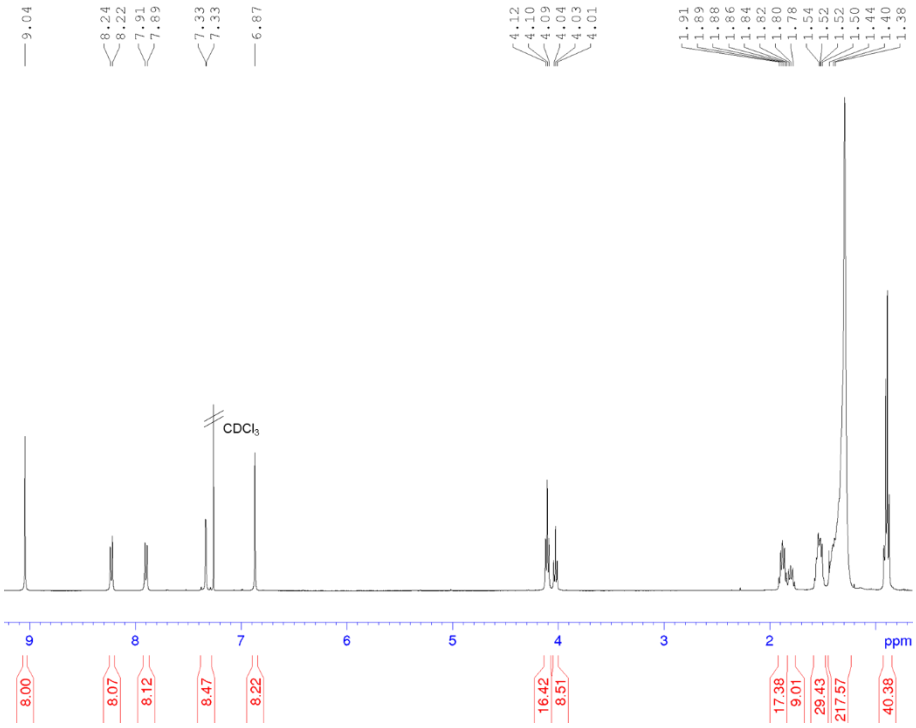
^{1}H NMR (400 MHz) spectrum of **3** in $CDCl_3$



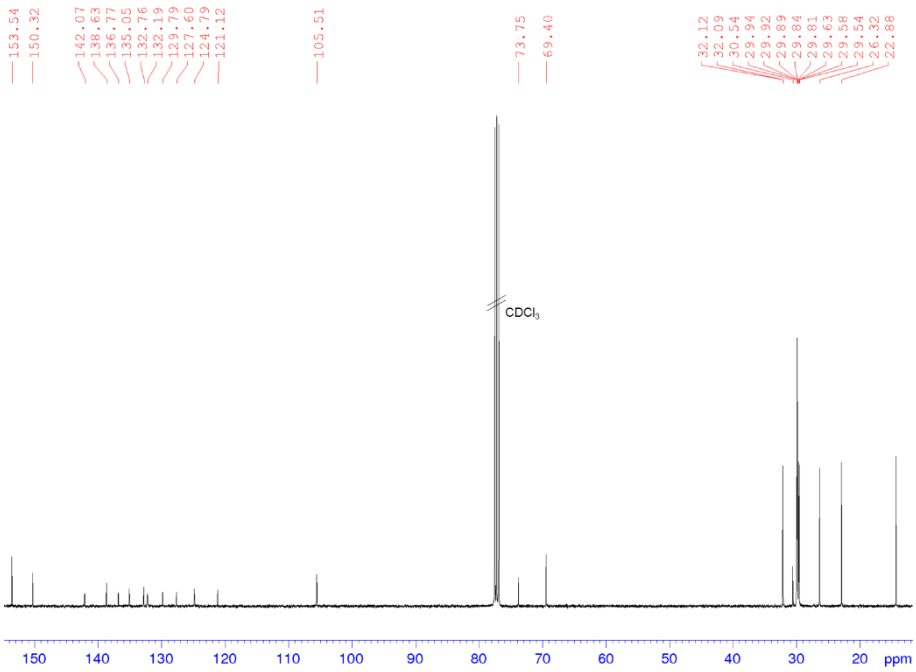
^{13}C NMR (100 MHz) spectrum of **3** in CD_2Cl_2



^{1}H NMR (400 MHz) spectrum of **4** in $CDCl_3$



^{13}C NMR (100 MHz) spectrum of **4** in $CDCl_3$



5) POM and XRS results for **1a**

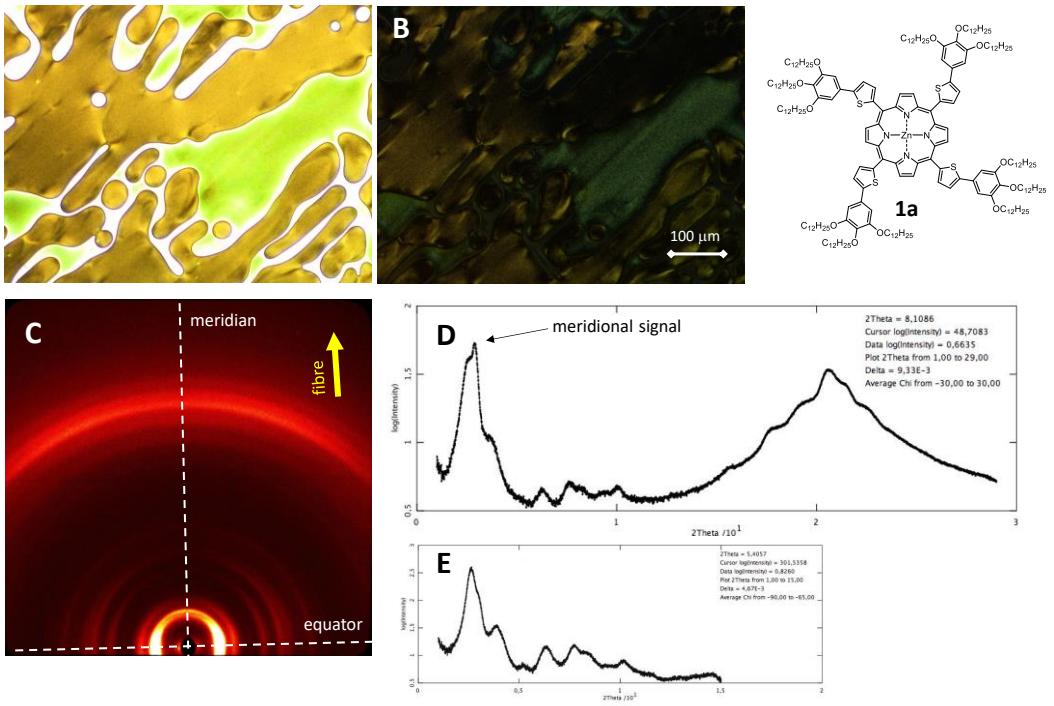


Figure S1. POM textures annealed for 60 hours (A, B). (A) Texture with a λ/4 compensator showing the thick and thin films and the areas without material. (B) Birefringence of the material, which reveals only after long annealing or shearing at ambient temperature. (C) XRS pattern of an extruded fibre of the soft crystalline phase of **1a** at 25 °C (yellow arrow shows the fibre direction). Integration along the meridian (D) and the equator (E) showing the reflection over the whole angular range pointing to a soft crystal.

6) DSC heating and cooling cycles for compounds **1**-**4**

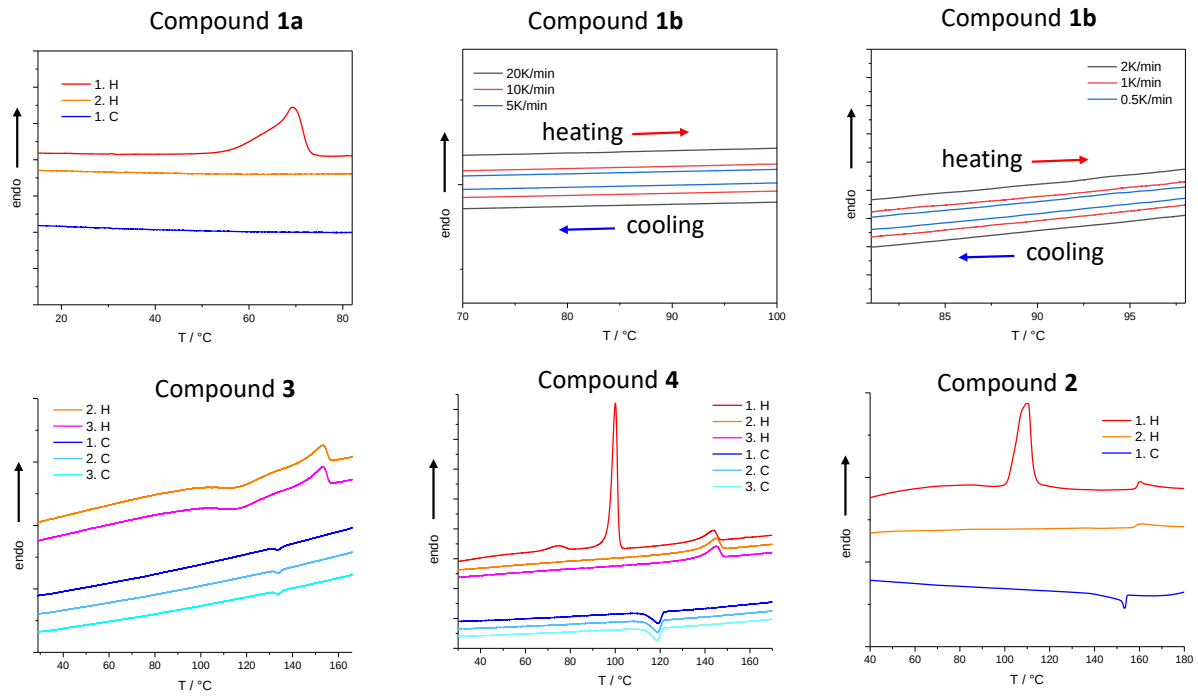


Figure S2. DSC heating and cooling cycles at a heating rate of 10 K / min. For compound **1b** the relevant temperature range was investigated by using various heating rates. However, the phase transition Col_h - I for **1b** did not show any sign in the DSC cycles.

7) Modelling

General

The LC phases were modeled with the program *BIOVIA Materials Studio 2017 R2*. The modelling is performed in the P1 unit cell without restrictions by symmetry elements. After the set-up of the unit cells the geometry optimization was first performed using the module "Forcite Plus (2017R2)" with the force field "COMPASSII" and the atom based summation method. Finally, the Ewald summation method has been applied, until the non-covalent interactions (electrostatic and van der Waals interactions) were large and negative.

*Mesophase of star mesogen **4***

The parameters for the orthorhombic unit cell was determined by XRS to be a = 83.5 Å, b = 48.0 Å and c = 69.6 Å. The latter parameter has been calculated assuming a double helical stacking producing the strongest signal on the second layer line (L = 2, see Figure 5). According to the highest experimental density 1.039 gcm^{-3} a minimum of Z = 53 molecules fill the unit cell. Since the experimental density is only a minimum density estimate and the orthorhombic cell needs two columns with an integer number of dimers, the total number of mesogens in the cell must be Z = 4n. Consequently, 56 mesogens were taken to fill the cell, which are shared by two columns (28 molecules, i.e. 14 dimers in each column). The dimers are separated by 4.97 Å and rotated by 25.71° along the columnar axis. This generates the double helix with a pitch of 69.6 Å. The whole column is then copied and shifted by 1/2a, 1/2b and 1/2c to obtain the body-centred cell. Geometry optimization affords van der Waals interactions of -36 663 kJ/mol (-655 kJ/mol corresponding to a single mesogen) and electrostatic interactions of -160 872 kJ/mol (-2873 kJ/mol corresponding to a mesogen). The latter consist mainly of the interaction between Zn^{2+} and the nitrogens. Considering only van der Waals interaction the stabilization energy amounts to about 1.4 single C-C bonds. This rationalizes the stability of the stacking model.

8) Results from DFT energy minimization for compounds **1b** and **4**

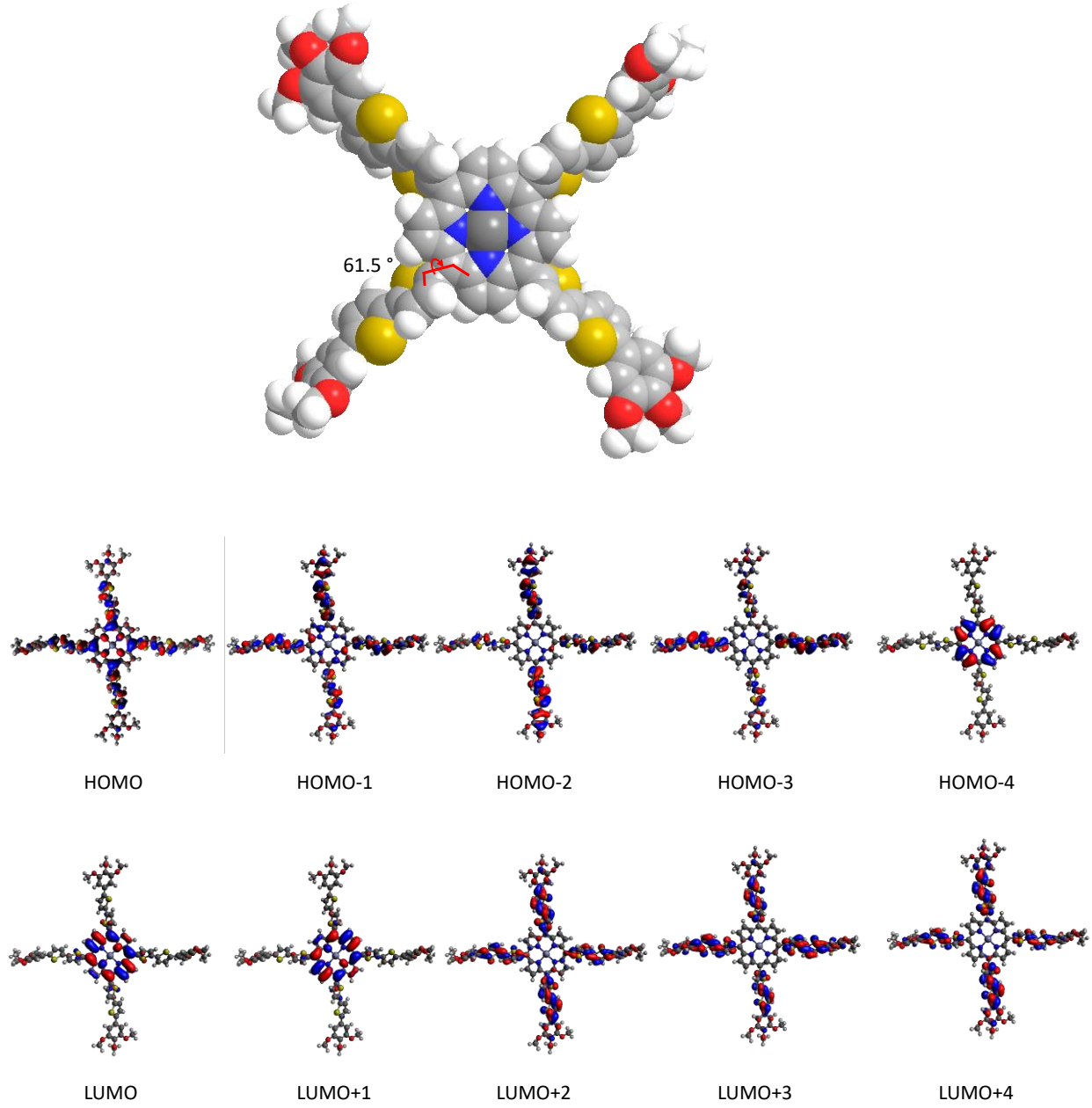


Figure S3. Space-filling, geometry optimized structure of compound **1b** and the associated frontier orbitals (HOMO and LUMO). The peripheral chains have been reduced to methyl groups for DFT calculations. The average dihedral angle between the thiophene ring and the core amounts to 61.6 °.

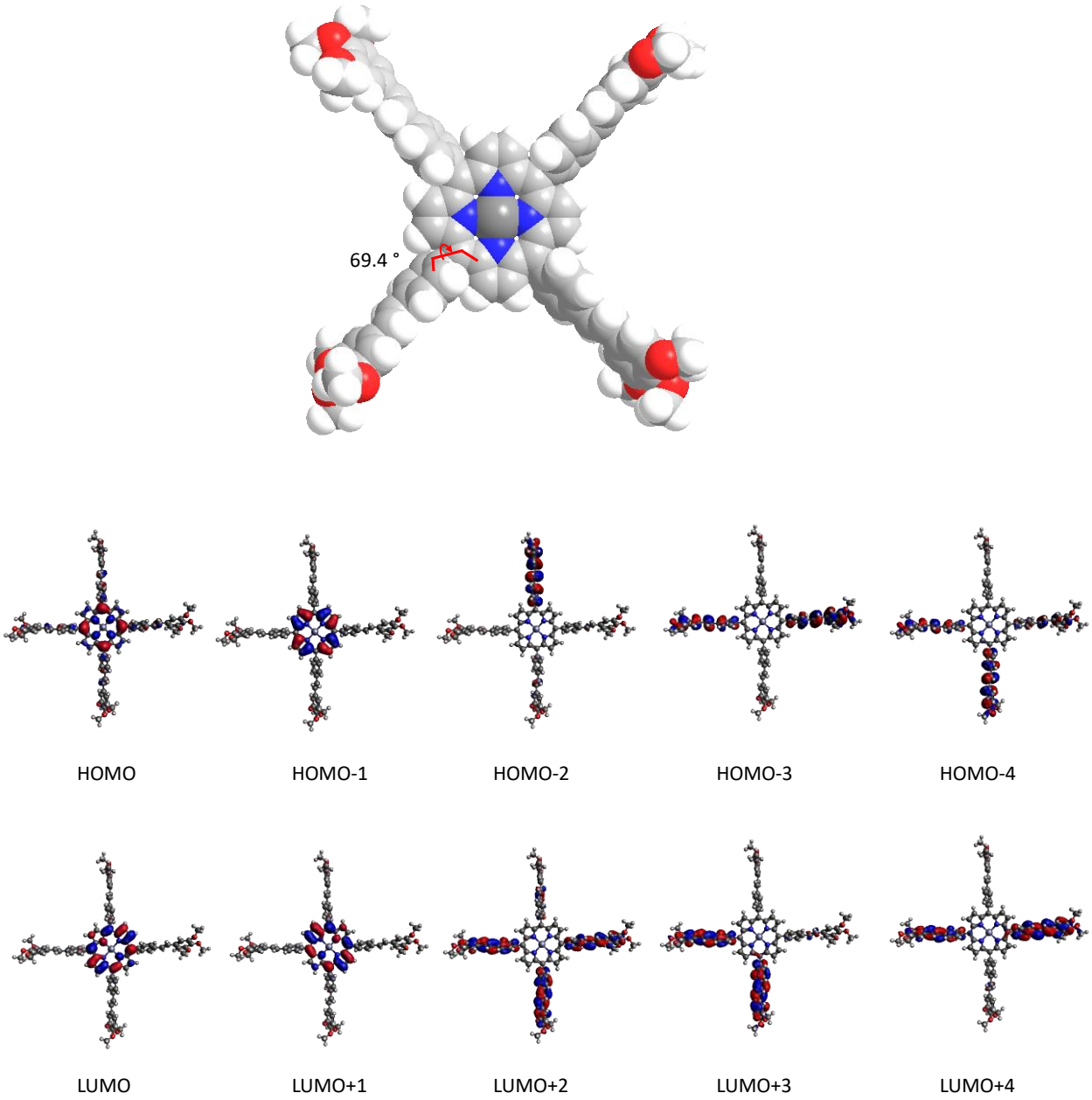


Figure S4. Space-filling, geometry optimized structure of compound **4** and the associated frontier orbitals (HOMO and LUMO). The peripheral chains have been reduced to methyl groups for DFT calculations. The average dihedral angle between the phenyl ring and the core amounts to 69.3 °.

Table S1. Calculated energies of the first five HOMO and LUMO levels for the compound **1b**.

Compound	**HOMO** [eV]		**LUMO** [eV]	
Compound **1b**	HOMO	-4.810	LUMO	-2.351
	HOMO -1	-5.098	LUMO +1	-2.333
	HOMO -2	-5.112	LUMO +2	-1.498
	HOMO -3	-5.135	LUMO +3	-1.435
	HOMO -4	-5.260	LUMO +4	-1.414
Compound **4**	HOMO	-4.903	LUMO	-2.138
	HOMO -1	-5.136	LUMO +1	-2.134
	HOMO -2	-5.292	LUMO +2	-1.405
	HOMO -3	-5.337	LUMO +3	-1.349
	HOMO -4	-5.348	LUMO +4	-1.337

Table S2. Results from the Gaussian calculations for the compound **1b**.

Compound	**1b**	**4**
Calculation Method	RB3LYP	RB3LYP
Basis Set	6-31G(D)	6-31G(D)
Charge	0	0
Spin	Singlet	Singlet
Electronic Energie	-9480.511508 Hartee	-6299.846951 Hartee
Imaginary Freq.	0	0
Dipole Moment	7.236021 Debye	3.501685 Debye

Compound 1b

```
#p freq b3lyp/6-31g(d) formcheck scf=(maxcycle=250,tight) symmetry=none

1b freq

0 1
C 17.05911021 24.10750271 2.66528119
C 16.71536921 22.79173465 2.63308719
C 15.28349712 22.73387664 2.46001118
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C 14.53809603 21.54057855 2.37797217
C 13.13024393 21.47582954 2.33585117
```

C 12.37325890 20.26260248 2.13844315
C 11.05723381 20.60571048 2.16773316
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C 9.80359270 22.77488861 2.48491818
C 9.73964972 24.17906875 2.58750019
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Compound 4

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