Supporting Information

Click Procedure of Phthalocyanine Star-Shaped Mesogens – the Effect of Size and Spacer Length
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1) Materials

All commercial materials employed were used as received, without further purification. P(OEt)$_3$ was freshly distilled under reduced pressure and solvents were distilled and dried via standard procedures.

2) 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 mL-min$^{-1}$. NMR spectra were recorded on a Bruker-Daltonics Avance-400 spectrometer operating at 400 MHz ($_1^H$) or 100 MHz ($^{13}C$) or on a Bruker-Daltonics Ascend-600 operating at 600 MHz ($_1^H$) or 151 MHz ($^{13}C$), with the residual solvent signal used as the internal standard. Mass spectra were recorded on a Bruker-Daltonics autfleX II (MALDI), on a Bruker-Daltonics ultrafleXtreme (HRMS-MALDI) and on a Bruker-Daltonics microTOF focus (HRMS-ESI). Elemental analysis experiments were performed at the Institute of Inorganic Chemistry, University of Würzburg. 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. UV-Vis- absorption studies in solution were performed with a JASCO V-770. Emission studies in solution were realized with an Edinburgh Instruments FLS980. The temperature dependent SAXS and WAXS X-ray investigations were performed on a Bruker Nanostar (Detector Vantec2000, Microfocus copper anode X-ray tube Incoatec). The aligned fibers were transferred to Mark capillaries, which were sealed and glued into the metal sample holder. The XRS heating system was calibrated by liquid crystal standard compounds.
3) Synthesis

The synthesis of the headgroup 3, the functionalized repeating unit 11 and the core-precursor 9 were carried out according to the literature.\(^1\) The fullerene with spacer 16 was synthesized according to the literature.\(^2\)

![Scheme S1. Synthesis of the phthalocyanine 1b.](image)

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\(^1\) M. Lehmann, M. Dechant, M. Holzapfel, A. Schmiedel, C. Lambert, *Angew. Chem. Int. Ed.* 2019, 58, 3610.

\(^2\) M. Lehmann, M. Dechant, M. Hügel, N. Scheuring, T. Ghosh, *Chem. Eur. J.* 2019, 25, 3352-3361.
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11 1) KO\textsubscript{Bu}, THF, 11
2) LiAlH\textsubscript{4}, THF
3) MnO\textsubscript{2}, EtOAc

12; 60 %

9 KO\textsubscript{Bu}, THF, 5

13; 85 %

Pd(PPh\textsubscript{3})\textsubscript{4}, Morpholin
THF

15; 44 %

R = (CH\textsubscript{2}CH\textsubscript{2}O)\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}

14; 94 %
**Scheme S2.** Synthesis of phthalocyanine 2b.

**Scheme S3.** Synthesis of fullerene with spacer 16.
Synthetic Procedures

\((E)\text{-}{2-((4\text{-}(3,4,5\text{-Tris}(2\text{-}(2\text{-ethoxyethoxy})ethoxy)ethoxy)styryl)benzyl)oxy)tetrahydro-2H-pyrane} (5)\)

\[
\begin{align*}
\text{H}_3\text{CCH}_2\text{C(OH}_2\text{CH}_2\text{C}_3\text{O} & \quad \text{O}\text{(CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_3 \\
\text{O}\text{(CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_3 & \quad \text{O}
\end{align*}
\]

3.49 g (31.1 mmol) KO\text{Bu} was added in portions to a stirred solution of 10.0 g (13.2 mmol) 3 and 3.78 g (17.2 mmol) 4 in 15 mL dry THF under nitrogen atmosphere at 0 °C. After complete reaction, the solvent was removed under reduced pressure and the crude product subjected to column chromatography (silica, EtOAc : MeOH = 10 : 1 (v/v)), to yield 9.69 g (11.8 mmol, 89 %) of a brown oil, which was used in the next step without further purification.

\(^1\text{H} \text{NMR (400 MHz, CDCl}_3\text{): } \delta = 1.22 (t, ^3\text{J} = 7.0 \text{ Hz}, 6 \text{ H, CH}_3), 1.23 (t, ^3\text{J} = 7.1 \text{ Hz}, 3 \text{ H, CH}_3), 3.54 (q, ^3\text{J} = 7.0 \text{ Hz}, 4 \text{ H, CH}_2), 3.54 (q, ^3\text{J} = 7.0 \text{ Hz}, 2 \text{ H, CH}_2), 3.60-3.78 (m, 25 \text{ H, CH}_2), 3.81-3.84 (m, 2 \text{ H, CH}_2), 3.89-3.91 (m, 4 \text{ H, CH}_2), 3.93-3.98 (m, 1 \text{ H, CH}_2), 4.17-4.25 (m, 6 \text{ H, CH}_2), 4.53 (d, ^2\text{J} = 12.1 \text{ Hz}, 1 \text{ H, CH}_2P), 4.73-4.75 (m, 1\text{H, OCH}_3), 4.81 (d, ^2\text{J} = 12.1 \text{ Hz}, 1 \text{ H, CH}_2P), 6.78 (s, 2 \text{ H, aromat. H}), 6.99 (m, 2 \text{ H, olefin. H}), 7.38 (AA'BB', 2 \text{ H, aromat. H}), 7.49 (AA'BB', 2 \text{ H, aromat. H}) \text{ ppm.}
\]
(E)-Diethyl-(4-(3,4,5-tris(2-(2-ethoxyethoxy)ethoxy)ethoxy)styryl)benzyl)phosphonate (6)

4.80 g (5.99 mmol) 5 were dissolved in 1.74 ml (1.69 g, 10.1 mmol) triethylphosphite under nitrogen atmosphere and the mixture was heated to 130 °C for three hours. The solvent was removed under reduced pressure and the crude product purified by column chromatography (silica, EtOAc : MeOH = 10 : 1 (v/v)) to yield 3.71 g (4.32 mmol, 72 %) of a yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 1.20$ (t, $^3J = 7.0$ Hz, 9 H, CH$_3$), 1.25 (t, $^3J = 7.1$ Hz, 6 H, CH$_3$), 3.16 (d, $^2J_{P,H} = 21.8$ Hz, 2 H, PCH$_2$), 3.52 (q, $^3J = 7.0$ Hz, 4 H, CH$_2$), 3.57-3.76 (m, 24 H, CH$_2$), 3.80 (t, $^3J = 5.1$ Hz, 2 H, CH$_2$), 3.87 (t, $^3J = 5.0$ Hz, 4 H, CH$_2$), 3.98-4.07 (m, 4 H, CH$_2$), 4.16 (t, $^3J = 5.1$ Hz, 2 H, CH$_2$), 4.21 (t, $^3J = 5.0$ Hz, 4 H, CH$_2$), 6.75 (s, 2 H, aromat. H), 6.95 (m, 2 H, olefin. H), 7.28 (AA'BB', 2 H, aromat. H), 7.43 (AA'BB', 2 H, aromat. H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 15.4, 16.6$ (CH$_3$), 33.8, 62.4, 66.8, 69.1, 70.1, 70.2, 70.8, 70.9, 70.9(8), 71.0(2), 71.1, 72.8 (CS), 106.0, 126.8, 127.9, 128.6, 130.5 (CT), 131.8, 133.2, 136.2, 138.5, 153.2 (Cq) ppm.

MALDI-HRMS: m/z: calcd.: 858.4525 [M]$^+$, found: 858.4524 [M]$^+$. 

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(E,E)-4-(4-(3,4,5-Tris(2-(2-ethoxyethoxy)ethoxy)ethoxy)styryl)styryl)benzaldehyde (8)

153 mg (1.36 mmol) KOtBu was added in portions to a stirred solution of 900 mg (1.05 mmol) phosphonate 6 and 240 mg (1.15 mmol) 4-((diethoxymethyl)benzaldehyde in 15 mL dry THF under nitrogen atmosphere at 0 °C. After stirring overnight, the reaction was quenched with 2N HCl. The aqueous layer was extracted with EtOAc, the combined organic layers dried over sodium sulfate and the solvent removed under reduced pressure. The crude product was purified by column chromatography (silica, EtOAc : MeOH = 20 : 1 (v/v)) to yield 598 mg (713 µmol, 68 %) of an orange oil.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 1.20$ (t, $^3$J = 7.0 Hz, 6 H, CH$_3$), 1.20 (t, $^3$J = 7.0 Hz, 3 H, CH$_3$), 3.52 (q, $^3$J = 7.0 Hz, 4 H, CH$_2$), 3.52 (q, $^3$J = 7.0 Hz, 2 H, CH$_2$), 3.57-3.76 (m, 24 H, CH$_2$), 3.80 (t, $^3$J = 5.1 Hz, 2 H, CH$_2$), 3.88 (t, $^3$J = 5.1 Hz, 4 H, CH$_2$), 4.17 (t, $^3$J = 5.1 Hz, 2 H, CH$_2$), 4.22 (t, $^3$J = 5.10 Hz, 4 H, CH$_2$), 6.77 (s, 2 H, aromat. H), 6.97 (d, $^3$J = 16.3 Hz, 1 H, olefin. H), 7.03 (d, $^3$J = 16.3 Hz, 1 H, olefin. H), 7.16 (d, $^3$J = 16.3 Hz, 1 H, olefin. H), 7.27 (d, $^3$J = 16.3 Hz, 1 H, olefin. H), 7.51 (AA'BB', 2 H, aromat. H), 7.54 (AA'BB', 2 H, aromat. H), 7.66 (AA'BB', 2 H, aromat. H), 7.88 (AA'BB', 2 H, aromat. H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 15.3$ (Cp), 66.8, 69.1 69.9, 70.0, 70.7, 70.8, 71.0, 70.9, 72.6 (C$_6$), 106.6 (C$_6$, C-1), 127.0, 127.0, 127.2, 127.4, 127.6, 129.1, 130.4, 131.9 (C$_6$), 132.9, 135.4, 135.9, 137.7, 138.8, 143.6, 153.0 (C$_6$), 191.8 (C$_6$) ppm.

MALDI-MS: m/z (%): calcd.: 838.45 ([M]$^+$, 100), found: 838.39 ([M]$^+$, 100).

MALDI-HRMS: m/z: calcd.: 861.4396 [M]$^+$, found: 861.4379 [M]$^+$.
(E,E,E)-4-(4-(3,4,5-Tris(2-(2-ethoxyethoxy)ethoxy)ethoxy)styryl)styryl)styryl)-phthalonitrile (10)

\[
\begin{align*}
\text{H}_2\text{C}_2\text{C(OH)CH}_2\text{C}_3\text{O}_3\text{CH}_2\text{CH}_3 &- \text{O(CH}_2\text{CH}_2\text{O)}_3\text{CH}_2\text{CH}_3
\end{align*}
\]

85.0 mg (760 µmol) KO\text{Bu} was added in portions to a stirred solution of 558 mg (665 µmol) aldehyde 8 and 176 mg (633 µmol) phosphonate 9 (Scheme S1) in 10 mL dry THF under nitrogen atmosphere at 0 °C. After stirring overnight, the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica, EtOAc : MeOH = 20 : 1 (v/v)) to yield 423 mg (439 µmol, 69 %) of an orange solid.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 1.20\) (t, \(3^J = 7.0\) Hz, 6 H, CH\(_3\)), 1.20 (t, \(3^J = 7.0\) Hz, 3 H, CH\(_3\)), 3.52 (q, \(3^J = 7.0\) Hz, 4 H, OCH\(_2\)), 3.52 (q, \(3^J = 7.0\) Hz, 2 H, OCH\(_2\)), 3.58-3.76 (m, 24 H, CH\(_2\)), 3.80 (t, \(3^J = 5.1\) Hz, 2 H, CH\(_2\)), 3.88 (t, \(3^J = 5.1\) Hz, 4 H, CH\(_2\)), 4.17 (t, \(3^J = 5.1\) Hz, 2 H, CH\(_2\)), 4.22 (t, \(3^J = 5.1\) Hz, 4 H, CH\(_2\)), 6.77 (s, 2 H, aromat. H), 6.96 (d, \(3^J = 16.2\) Hz, 1 H, olefin. H), 7.02 (d, \(3^J = 16.2\) Hz, 1 H, olefin. H), 7.07 (d, \(3^J = 16.3\) Hz, 1 H, olefin. H), 7.12 (d, \(3^J = 16.3\) Hz, 1 H, olefin. H), 7.17 (d, \(3^J = 16.3\) Hz, 1 H, olefin. H), 7.28 (d, \(3^J = 16.3\) Hz, 1 H, olefin. H), 7.49 (AA'BB', 2 H, aromat. H), 7.52 (AA'BB', 2 H, aromat. H), 7.54 (AA'BB', 2 H, aromat. H), 7.56 (AA'BB', 2 H, aromat. H), 7.76 (m, 1 H, aromat. H), 7.80 (m, 1 H, aromat. H), 7.90 (m, 1 H, aromat. H) ppm.

\(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 15.3\) (C\(_p\)), 66.8, 69.0, 69.9, 70.0, 70.7, 70.8(2), 70.8(4), 71.0, 70.7 72.6 (C\(_a\)), 106.5 (C\(_i\)), 113.3, 115.6, 115.8, 116.6 (C\(_q\)), 124.3, 127.0, 127.2, 127.2, 127.7, 127.7, 128.8, 128.9, 130.3 131.0 (C\(_i\)), 132.9 (C\(_q\)), 134.0, 134.7 (C\(_i\)), 134.8, 136.4, 137.1, 138.7, 138.8, 142.9, 152.9 (C\(_q\)) ppm.

MALDI-MS: m/z (%): calcd.: 985.48 ([M+Na]\(^+\), 100), found: 985.51 ([M+Na]\(^+\), 100).
ESI-HRMS: m/z: calcd.: 1001.4560 [M+K]+, found: 1011.4574 [M+K]+.

Melting point: 91 °C.

(all-E)-(SP-4-1)-(Tetra[4-(3,4,5-(2-(2-ethoxyethoxy)ethoxy)ethoxy)styryl]styryl)styryl]-29H,31H-phthalocyaninato(2-)·κN²⁻¹,κN³⁻¹,κN⁴⁻¹,κN⁵⁻¹zinc (1b) (mixture of regioisomers)

357 mg (372 µmol) 10 and 40.6 mg (185 µmol) Zn(OAc)₂·2H₂O were dissolved in 5 mL DMAE and stirred under nitrogen atmosphere at 140 °C. After 24 hours, the solvent was removed under reduced pressure and the crude product purified by column chromatography (silica, EtOAc : MeOH = 3 : 1 (v/v)). The resulting green solid was subjected to preparative recycling GPC and precipitated three times from CH₂Cl₂ solution with n-hexane to yield 110 mg (28.0 µmol, 31 %) of a green solid.

¹H NMR (400.1 MHz, THF-d₈): δ = 1.16-1.20 (m, 36 H, CH₃), 3.47 (m, 24 H, OCH₂), 3.54-3.86 (m, 96 H, CH₂), 3.81 (bs, 8 H, CH₂), 3.86 (bs, 16 H, CH₂), 4.18-4.23 (m, 24 H, CH₂), 6.91 (s, 8 H, aromat. H), 7.13 (s, 8 H, olefin. H), 7.32 (bs, 8 H, aromat./olefin. H), 7.56-7.69 (m, 24 H,
aromat./olefin. H), 7.87-7.91 (m, 16 H, aromat./olefin. H), 8.05-8.11 (bs, 4 H, aromat. H), 8.60-9.12 (bs, 8 H, aromat. H) ppm.

$^{13}$C NMR (100 MHz, THF-$d_8$): $\delta = 16.0$ (C$_p$), 67.3, 70.1, 70.9, 71.7, 71.2, 71.7, 71.8, 71.9, 73.6 (C$_a$), 107.3, 121.9, 123.5 127.9, 128.1, 128.3, 129.9, 128.5, 129.2, 129.3, 130.3 (C$_t$), 133.9, 137.8, 138.2, 138.3, 138.4, 140.1, 153.6 154.2 (C$_q$) ppm.

Several quaternary and tertiary signals, especially of the phthalocyanine core and the arms of low intensity could not be identified certainly due to aggregation and the presence of four regioisomers. Moreover, only very broad signals could be obtained, for which reason, $^{13}$C spectra are often omitted in the literature or only selected peaks are assigned.

MALDI-HRMS: m/z: calcd.: 3913.9001 [M]$^+$, found: 3913.8896[M]$^+$.

UV-Vis (CHCl$_3$): $\lambda$ max, $\varepsilon/10^4$): 387 (23.80), 646(4.60), 717 (22.02) nm.

FTIR: $\tilde{\nu}$ [cm$^{-1}$]: 829.2, 954.6 (s, $E$-C=C), 1047.2, 1090.6 (s, C-O-C), 1245.8, 1341.3, 1394.3, (C-H), 1430.0, 1487.8 (w, -CH$_3$), 1576.5 (s, C=C), 2862.8, 2922.6, 2968.9 (s, -CH$_3$), 3022.9 (w, C$_{Ar}$-H).

Elemental analysis (%) for C$_{224}$H$_{281}$N$_8$O$_{48}$Zn calcd.: C 68.65, H 7.23, N 2.86 found: C 63.7, H 6.86, N 2.64. see comment [A] page 19

Melting point: Decomposition > 350°C.

$^{(E,E)}$-3-allyloxy-4-(4-(3,4,5-tris(2-(2-ethoxyethoxy)ethoxy)ethoxy)styryl)styryl)-benzaldehyde (12)

450 mg (4.01 mmol) KO'Bu were added in portions to a mixture of 1.92 g (2.23 mmol) phosphonate 6 and 588 mg (2.67 mmol) aldehyde 11 (Scheme S2) in dry THF under nitrogen atmosphere at 0 °C. After stirring overnight, water and 1M HCl were added. The aqueous layer was extracted with chloroform, the combined organic layers dried over sodium sulphate and
the solvent removed under reduced pressure. The crude product was purified by column chromatography (silica, EtOAc : MeOH = 10 : 1 (v/v)) to yield 2.01 g (2.17 mmol, 97%) of a yellow oil. Without further purification, the product was dissolved in dry THF under nitrogen atmosphere and 105 mg (2.77 mmol) LiAlH₄ were added at 0 °C. After stirring overnight at room temperature, H₂O dest. and 1 M HCl were added. The aqueous layer was extracted with DCM, the combined organic layers dried over sodium sulfate and the solvent removed under reduces pressure. The crude product was purified by column chromatography (silica, EtOAc : MeOH = 15 : 1 (v/v)) to yield 1.76 g (1.96 mmol, 71%) of an orange oil, which was used without further purification in the next step.

(E,E)-3-allyloxy-4-(4-(3,4,5-tri(2-[2-(2-ethoxyethoxy)ethoxy]ethoxy)styryl)styryl)benzylalcohol

1H NMR (400 MHz, CDCl₃): δ = 1.20 (t, 3J = 7.0 Hz, 6 H, CH₃), 1.20 (t, 3J = 7.0 Hz, 3 H, CH₃), 3.52 (q, 3J = 7.0 Hz, 4 H, CH₂), 3.52 (q, 3J = 7.0 Hz, 2 H, CH₂), 3.57-3.76 (m, 24 H, CH₂), 3.80 (t, 3J = 5.3 Hz, 2 H, CH₂), 3.88 (t, 3J = 5.1 Hz, 4 H, CH₂), 4.17 (t, 3J = 5.1 Hz, 2 H, CH₂), 4.22 (t, 3J = 5.1 Hz, 4 H, CH₂), 4.64 (td, 3J = 5.1 Hz; 4J = 1.6 Hz, 2 H, CH₂), 4.69 (s, 2 H, ArCH₂), 5.33 (qd, 3J = 10.5 Hz; 4J = 1.5 Hz, 1 H, olefin. H), 5.47 (qd, 3J = 17.2 Hz; 4J = 1.7 Hz, 1 H, olefin. H), 6.08-6.18 (m, 1 H, olefin. H), 6.76 (s, 2 H, aromat. H), 6.94-6.96 (m, 2 H, aromat. H), 6.95 (d, 3J = 16.2 Hz, 1 H, olefin. H), 7.00 (d, 3J = 16.2 Hz, 1 H, olefin. H), 7.12 (d, 3J = 16.4 Hz, 1 H, olefin. H), 7.47 (AA′BB′, 2 H, aromat. H), 7.51 (AA′BB′, 2 H, aromat. H), 7.51 (d, 3J = 16.4 Hz, 1 H, olefin. H), 7.59 (d, 3J = 7.7 Hz, 1 H, aromat. H) ppm.

13C NMR (100 MHz, CDCl₃): δ = 15.3 (C₆), 65.4, 66.8, 69.0, 69.4, 69.9, 70.0, 70.7, 70.8(2), 70.8(3), 70.9, 71.0, 72.5 (C₆), 106.4 (C₁, C-1), 111.1 (C₁), 117.6 (C₆), 119.5, 123.2 (C₁), 126.2 (C₆), 126.7, 126.8, 127.0, 128.0, 128.3, 128.7 (C₆), 133.1 (C₆), 133.4 (C₁), 136.5, 137.4, 138.5, 141.1, 152.9, 156.3 (C₆) ppm.

MALDI-MS: m/z (%): calcd.: 896.49 ([M]+, 100), found: 896.42 ([M]+ 100).

454 mg (5.22 mmol) MnO₂ and 781 mg (871 μmol) of the benzylalcohol were dissolved in DCM and stirred at room temperature for four days. The mixture was filtered over celite, the solvent removed under reduced and the crude product purified by column chromatography (silica, EtOAc : MeOH = 10 : 1 (v/v)) to yield 677 mg (756 μmol, 87%) of aldehyde 12 as an orange oil.

1H NMR (400.1 MHz, CDCl₃): δ = 1.20 (t, 3J = 7.0 Hz, 6 H, CH₃), 1.20 (t, 3J = 7.0 Hz, 2 H, CH₂), 3.52 (q, 3J = 7.0 Hz, 4 H, CH₂), 3.52 (q, 3J = 7.0 Hz, 2 H, CH₂), 3.80 (t, 3J = 5.1 Hz, 2 H, CH₂), 3.88 (t, 3J = 5.1 Hz, 4 H, CH₂), 4.17 (t, 3J = 5.1 Hz, 2 H, CH₂), 4.22 (t, 3J = 5.1 Hz, 4 H, CH₂), 4.71 (td, 3J = 5.1 Hz; 4J = 1.5 Hz, 2 H, CH₂), 5.36 (ddt, 3J = 10.5 Hz; 4J = 1.5 Hz, 1 H, olefin. H), 5.49 (ddt, 3J = 17.3 Hz; 4J = 1.6 Hz, 1 H, olefin. H), 6.09-6.19 (m, 1 H, olefin. H), 6.77 (s, 2 H, aromat. H), 6.97 (d, 3J = 16.0 Hz, 1 H, olefin. H), 7.02 (d, 3J = 16.2 Hz, 1 H, olefin. H), 7.28 (d, 3J = 16.5 Hz, 1 H, olefin. H), 7.40 (d, 4J = 1.4 Hz, 1 H, aromat. H), 7.47 (dd, 3J = 8.0 Hz; 4J = 1.4 Hz, 1 H, aromat. H), 7.50 (AA′BB′, 2 H, aromat. H), 7.55 (AA′BB′, 2 H, aromat. H), 7.55 - 12 -
Hz (d, $^3J = 16.5$ Hz, 1 H, olefin. H), 7.77 (d, $^3J = 7.7$ Hz, 1 H, aromat. H), 9.95 (s, 1 H, CHO) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 15.3$ (C$_p$), 66.8, 69.1, 69.5, 69.9, 70.0, 70.7, 70.8, 70.9, 71.0, 72.6 (C$_s$), 106.6 (C$_t$), 111.0 (C$_s$), 118.1 (C$_s$), 122.3, 124.5, 126.7, 126.9, 127.5, 127.8, 128.9, 132.1, 132.8 (C$_t$), 132.9, 133.4, 136.4, 136.6, 137.4, 138.7, 153.0, 156.3 (C$_q$), 191.7 (C$_t$) ppm. MALDI-MS: m/z (%): calcd.: 894.48 ([M]+•, 100), found: 894.45 ([M] +•, 100). MALDI- HRMS: m/z: calcd.: 894.4760 [M]+•, found: 894.4746 [M]+•.

(E,E,E)-3-allyloxy-4-(4-(4-(3,4,5-tris(2-ethoxyethoxy)ethoxy)ethoxy)styryl)-styryl)styryl]phthalonitrile (13)

77.7 mg (694 µmol) KO'Bu were added in portions to a mixture of 543 mg (607 µmol) aldehyde 12 and 160 mg (578 µmol) phosphonate 9 in dry THF under nitrogen atmosphere at 0 °C. After stirring overnight at room temperature, the solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica, EtOAc : MeOH = 10 : 1 (v/v)) to yield 501 mg (492 µmol, 85 %) of a red solid.

$^1$H NMR (400.1 MHz, CDCl$_3$): $\delta = 1.20$ (t, $^3J = 7.00$ Hz, 6 H, CH$_3$), 1.21 (t, $^3J = 7.1$ Hz, 2 H, CH$_3$), 3.52 (q, $^3J = 7.0$ Hz, 4 H, CH$_2$), 3.52 (q, $^3J = 7.0$ Hz, 2 H, CH$_2$), 3.80 (t, $^3J = 5.2$ Hz, 2 H, CH$_2$), 3.88 (t, $^3J = 5.3$ Hz, 4 H, CH$_2$), 4.17 (t, $^3J = 5.3$ Hz, 2 H, CH$_2$), 4.22 (t, $^3J = 5.1$ Hz, 4 H, CH$_2$), 4.70 (dt, $^3J = 5.1$ Hz; $^4J = 1.6$ Hz, 2 H, CH$_2$), 5.38 (overlapped ddt, $^3J = 10.5$ Hz; $^4J = 1.5$ Hz, $^4J = 1.5$ Hz, 1 H, olefin. H), 5.51 (overlapped ddt, $^3J = 17.3$ Hz; $^4J = 1.6$ Hz, 1 H, olefin. H), 6.11-6.21 (m, 1 H, olefin. H), 6.77 (s, 2 H, aromat. H), 6.96 (d, $^3J = 16.4$ Hz, 1 H, olefin. H), 7.77 (d, $^3J = 7.7$ Hz, 1 H, aromat. H), 9.95 (s, 1 H, CHO) ppm.
7.01 (d, 3J = 16.4 Hz, 1 H, olefin. H), 7.04 (d, 4J = 1.4 Hz, 1 H, aromat. H), 7.04 (d, 3J = 16.2 Hz, 1 H, olefin. H), 7.17-7.20 (m, 1 H, aromat. H), 7.20 (d, 3J = 16.6 Hz, 1 H, olefin. H), 7.26 (d, 3J = 16.2 Hz, 1 H, olefin. H), 7.49 (AA’BB’, 2 H, aromat. H), 7.53 (AA’BB’, 2 H, aromat. H), 7.53 (d, 3J = 8.4 Hz, 1 H, aromat. H), 7.80 (dd, 3J = 8.4 Hz, 4J = 1.6 Hz 1 H, aromat. H), 7.91 (d, 3J = 1.6 Hz, 1 H, aromat. H) ppm.

13C NMR (100 MHz, CDCl3): δ = 15.3 (Cp), 66.8, 69.1, 69.5, 69.9, 70.0, 70.7, 70.8, 70.9, 71.0, 72.6 (Cs, C°OCH2), 106.5, 111.0 (Ci) 113.3, 115.6, 115.8, 116.6 (Cu), 117.9 (Cs), 120.5 122.6, 124.3, 126.9, 127.2, 127.9, 128.5, 128.6 (Ct), 129.9 (Cu), 130.4, 131.1 (Ci), 133.0 (Cu), 133.2, 134.0, 134.9 (Ct), 135.8, 136.9, 137.1, 138.7, 142.8, 153.0, 156.3 (Cu) ppm.

MALDI-MS: m/z (%): calcd.: 1018.52 ([M]+•, 100), found: 1018.53 ([M]+•, 100).

ESI-HRMS: m/z: calcd.: 1041.50831 [M+Na]+, found: 1041.50842 [M+Na]+.

Melting point: 101 °C.

(E,E,E)-3-hydroxy-4-(4-(4-(3,4,5-tris(2-(2-ethoxyethoxy)ethoxy)ethoxy)styryl)-styryl)styryl)phthalonitrile (14)

450 mg (440 µmol) of the protected compound 13 were dissolved in dry THF under nitrogen atmosphere. After degassing with nitrogen, 25.0 mg (21.6 µmol) Pd(PPh3)4 and 154 µL (157 mg, 1.80 mmol) morpholine were added and the mixture was stirred for two hours at room temperature. After complete reaction, 1M HCl was added and the aqueous layer extracted with DCM. The combined organic layers were dried over sodium sulphate and the solvent was
removed under reduced pressure. The crude product was purified by column chromatography (silica, EtOAc : MeOH = 10 : 1 (v/v)) to yield 403 mg (412 µmol, 94%) of a red oil.

\[ ^1H \text{NMR (400.1 MHz, CDCl}_3\text{): } \delta = 1.20 \text{ (t, }^3J = 7.0 \text{ Hz, } 6 \text{ H, } \text{CH}_2\text{)}, 1.20 \text{ (t, }^3J = 6.9 \text{ Hz, } 3 \text{ H, } \text{CH}_3\text{), 3.52 \text{ (q, }^3J = 7.0 \text{ Hz, } 6 \text{ H, } \text{CH}_2\text{), 3.57-3.76 (m, } 24 \text{ H, } \text{CH}_2\text{), 3.79 \text{ (t, }^3J = 5.1 \text{ Hz, } 2 \text{ H, } \text{CH}_2\text{), 3.86 \text{ (t, }^3J = 5.1 \text{ Hz, } 4 \text{ H, } \text{CH}_2\text{), 4.16 \text{ (t, }^3J = 5.1 \text{ Hz, } 2 \text{ H, } \text{CH}_2\text{), 4.20 \text{ (t, }^3J = 5.1 \text{ Hz, } 4 \text{ H, } \text{CH}_2\text{), 5.84 (bs, } 1 \text{ H, } \text{OH}\text{), 6.74 (s, } 2 \text{ H, aromat. H), } 6.93 \text{ (d, }^3J = 16.1 \text{ Hz, } 1 \text{ H, olefin. H), 6.98 \text{ (d, }^3J = 16.4 \text{ Hz, } 1 \text{ H, olefin. H), 7.01 \text{ (d, }^3J = 16.2 \text{ Hz, } 1 \text{ H, olefin. H), 7.02 \text{ (d, }^4J = 1.4 \text{ Hz, } 1 \text{ H, aromat. H), 7.12 \text{ (dd, }^3J = 7.9 \text{ Hz, }^4J = 1.2 \text{ Hz, } 1 \text{ H, aromat. H), 7.17 \text{ (d, }^3J = 16.4 \text{ Hz, } 1 \text{ H, olefin. H), 7.19 \text{ (d, }^3J = 16.2 \text{ Hz, } 1 \text{ H, olefin. H), 7.46, 7.51 (AA'BB', } 4 \text{ H, aromat. H), 7.56 \text{ (d, }^3J = 8.1 \text{ Hz, } 1 \text{ H, aromat. H), 7.74 \text{ (d, }^3J = 8.3 \text{ Hz, } 1 \text{ H, aromat. H), 7.77 \text{ (dd, }^3J = 8.3 \text{ Hz, }^4J = 1.4 \text{ Hz, } 1 \text{ H, aromat. H), 7.87 \text{ (d, }^4J = 1.4 \text{ Hz, } 1 \text{ H, H-7) ppm.}}\]

\[ ^{13}C \text{NMR (100 MHz, CDCl}_3\text{): } \delta = 15.3 \text{ (C}_p\text{), 66.8, 68.9, 69.8(9), 69.9(3), 70.6, 70.7, 70.8(1), 70.8(3), 70.9, 71.0, 72.5 \text{ (C}_b\text{), 106.3 \text{ (C}_t\text{), 113.1 \text{ (C}_a\text{), 114.7 \text{ (C}_t\text{), 115.6, 115.8, 116.4 \text{ (C}_a\text{), 120.1, 122.6, 124.4 \text{ (C}_t\text{), 126.3 \text{ (C}_a\text{), 126.9, 127.1, 127.3, 127.8, 129.9, 130.4, 131.1 \text{ (C}_a\text{), 133.1 \text{ (C}_a\text{), 133.9, 134.5 \text{ (C}_a\text{), 135.9, 136.8, 137.0, 138.4, 142.9, 152.8, 154.1 \text{ (C}_a\text{) ppm.}}\]

ESI-HRMS: m/z: calcd.: 1001.4770 [M+Na]+, found: 1001.4747 [M+Na]+.

(E,E,E)-3-((tetrahydro-2H-pyran-2-yl)oxy)-4-(4-(3,4,5-tris(2-(2-ethoxyethoxy)-ethoxy)ethoxy)styryl)styryl)styryl)phthalonitrile (15)

[Diagram of the molecule]

656 mg (670 µmol) phenol 14, 17.0 mg (67.0 µmol) PPTs and 121 µL (113 mg, 2.21 mmol) 3,4-dihydro-2H-pyran were dissolved in dry DCM under nitrogen atmosphere. After stirring at
room temperature for three days, saturated NaHCO₃-solution was added and the aqueous
layer was extracted with DCM. The combined organic layers were dried over sodium sulphate
and the solvent removed under reduced pressure. The crude product was purified by column
chromatography (silica, EtOAc : MeOH = 20 : 1 (v/v)) to yield 313 mg (294 µmol, 44 %) of an
orange solid.

¹H NMR (400.1 MHz, CD₂Cl₂): δ = 1.17(2) (t, 3J = 7.0 Hz, 6 H, CH₃), 1.17(4) (t, 3J = 7.0 Hz,
3 H, CH₃), 1.64-1.81 (m, 3 H, CH₂), 1.93-2.14 (m, 3 H, CH₂), 3.48(1) (q, 3J = 7.0 Hz, 4 H, CH₂),
3.48(4) (q, 3J = 7.0Hz, 4 H, CH₂), 3.53-3.72 (m, 25 H, CH₂), 3.77 (t, 3J = 5.0 Hz, 2 H,
C₃OCH₂CH₂), 3.87 (t, 3J = 4.9 Hz, 4 H, CH₂), 3.88-3.95 (m, 1 H, CH), 5.59 (t, 3J = 3.1 Hz, 1 H, CH),
6.80 (s, 2 H, aromat. H), 7.02 (d, 3J = 16.3 Hz, 1 H, olefin. H), 7.07 (d, 3J = 16.3 Hz; 1 H, olefin. H), 7.10 (d,
3J = 16.4 Hz, 1 H, olefin. H), 7.17 (d, 3J = 16.4 Hz, 1 H, olefin. H), 7.24 (m, 1 H, aromat. H),
7.25 (d, 3J = 16.5 Hz, 1 H, olefin. H), 7.30 (d, 3J = 16.4 Hz, 1 H, olefin. H), 7.37 (d, 4J = 1.3 Hz,
1 H, aromat. H), 7.51-7.59 (m, 5 H, olefin./aromat. H), 7.67 (d, 3J = 8.1 H, 1 H, aromat. H), 7.78
(d, 3J = 8.3 Hz; 1 H, aromat. H), 7.83 (d, 3J = 8.3 Hz; 4J = 1.5 Hz, 1 H, aromat. H), 7.93 (d,
4J = 1.5 Hz, 1 H, aromat. H) ppm.

¹³C NMR (100 MHz, CD₂Cl₂): δ = 15.4 (Cₚ), 19.3, 25.6, 30.8 , 62.4, 66.8, 69.1, 70.1, 70.8(5),
70.9(5), 70.9(8), 71.0(0), 71.0(3), 71.2, 72.8 (Cₜ), 97.0 (Cₜ), 106.1 (Cₜ), 113.4 (Cₜ), 114.2 (Cₜ),
116.0, 116.3, 116.7 (Cₜ), 121.2, 122.9, 124.8, 127.0, 127.1, 127.3 (Cₜ), 128.6 (Cₜ), 128.8,
129.9, 130.7, 131.4 (Cₜ), 133.2 (Cₜ), 134.2, 134.9 (Cₜ), 136.4, 137.2, 137.4, 138.7, 143.2, 153.2,
155.0 (Cₚ) ppm.

ESI-HRMS: m/z: calcd.: 1085.5345 [M+Na]^+, found: 1085.5349 [M+Na]^+.

Melting point: 74 °C.
(all-E)-(SP-4-1)-(Tetra[4-(3,4,5-tri[2-(2-ethoxyethoxy)ethoxy]ethoxy)styryl]styryl)-3-(2'H-[5,6]fullereno-C60-Ir[1,9-c]pyrrole-1',5'-dihydro-1'-methyl-2'-octylcarbonyloxy)styryl]-29H,31H-phthalocyaninato(2-)-κN29,κN30,κN31,κN32 zinc (2b) (mixture of regioisomers)

230 mg (219 µmol) 15, 19.2 mg (87.5 µmol) Zn(OAc)2·2(H2O) and three drops of DBU were dissolved in 4 mL DMAE and stirred under nitrogen atmosphere at 130 °C. After 12 hours, the solvent was removed under reduced pressure and the crude product was dissolved in dry DCM. At -78 °C, 60.0 µL (93.4 mg, 817 µmol) TFA were added and the solution was stirred for 50 minutes. The solvent was removed under reduced pressure and the crude product purified by column chromatography (silica, EtOAc : MeOH = 2 : 1 (v/v)) and subjected to preparative recycling GPC to yield 92.0 mg (32.1 µmol, 42 %) of a brownish-green solid.

HRMS-MALDI: m/z: calcd.: 3977.8798 [M]+, found: 3977.8983 [M]+

UV-Vis (CHCl3): λ max, (ε/104): 399 (21.45), 739 (2.20) nm.
FTIR: $\tilde{\nu}$ [cm$^{-1}$]: 829.2, 960.4 (s, $E$-C=C), 1047.2, 1091.5 (s, C-O-C), 1247.7, 1342.2, 1376.9 (C-H), 1430.9, 1505.2, 1580.4 (w, C=N), 1651.7 (s, C=C), 1721.2, 2852.2, 2919.7 (s, CH$_3$), 3200.3 (b, OH).

Without further purification, 45.0 mg (11.3 µmol) of this compound were dissolved in dry DCM. Under nitrogen atmosphere, of the synthesized compound, 57.5 mg (56.5 µmol) of DPTS and 38.5 µL (33.9 mg, 249 µmol) DIC were added and the reaction mixture was stirred for 20 days at room temperature. The solvent was removed under reduced pressure and the crude product purified by column chromatography (silica, EtOAc : MeOH = 10 : 1 (v/v)), subjected twice to preparative recycling GPC and precipitated three times from a mixture of DCM and MeOH to yield 15.0 mg (1.88 µmol, 17 %) of a brown-green solid.

$^1$H NMR (400.1 MHz, CD$_2$Cl$_2$ + 2 drops of pyridine-d$_5$): $\delta = 1.18$-2.00 (m, 130 H, CH$_2$), 2.20 (bs, 4 H, CH$_2$), 2.33 (bs, 4 H, CH$_2$), 2.79 (bs, 8 H, CH$_2$), 3.06 (bs, 12 H, NCH$_3$), 3.42-4.03 (m, 152 H, CH$_2$/C=), 4.19 (bs, 24 H, OCH$_2$), 4.60 (bs, 4 H, H-44), 6.83 (bs, 8 H, aromat. H), 6.98-7.93 (bm, 56 H, aromat./olefin. H), 9.17 (bs, 8 H, aromat. H).

Due to the size of the molecule, aggregation, the presence of regioisomers and four additional C$_{60}$-units, only very broad peaks could be obtained, which could only slightly be improved by high-temperature measurement and by addition of pyridine-d$_5$. Anyway, all relevant protons of the fullerene spacer and of the aromatic region could be identified. The broad signal at 4.60 ppm with an integration of four protons can be attributed to half of the diastereotopic protons of the CH$_2$ group within the pyrrolidine ring and confirms the successful and complete coupling of the four fullerene building block which is further supported by the mass spectra (Figure S7).

$^{13}$C NMR (151 MHz, CD$_2$Cl$_2$): $\delta = 15.6$ (C$_p$), 25.7, 27.5, 29.8, 30.0, 30.4, 31.1, 34.9 (C$_s$), 40.2 (C$_p$, NCH$_3$), 67.0, 69.5, 70.4, 71.1 (C$_s$), 70.4, 73.0 (C$_s$, OCH$_2$), 76.7 (C$_q$), 78.3 (C$_i$, NCH$_3$), 106.4 (C$_i$), 121.6, 126.2, 127.5, 128.2, 129.2 (C$_i$, aromat./olefin.-C), 133.3, 135.9, 136.2, 136.5, 137.3, 138.4, 139.8, 140.4, 142.0, 142.3, 143.3, 144.6, 145.4(0), 145.4(2), 145.8, 146.2, 146.5, 146.8, 147.4, 149.1, 153.1, 154.2, 154.9, 157.1 (C$_q$), 172.4 (C$_q$, COO) ppm.

Several quaternary and ternary signals, especially of the phthalocyanine core and the arms of low intensity could not be identified certainly, although a long time measurement at a 600-MHz-NMR-spectrometer with a highly sensitive cryoprobe was performed. Anyway, the signals at 40.2 ppm and 78.3 ppm are characteristic for the pyrrolidine ring of the fullerene spacer derivative, and many signals between 157.8-133.6 ppm and the signal of the ester at 172.4 ppm show the presence of the fullerene spacers attached to the phthalocyanine star mesogen.

UV-Vis (CHCl$_3$): $\lambda_{\text{max}}$ (ε/10$^4$): 255 (47.26), 325 (21.92), 384 (23.31), 723 (4.88) nm.

MALDI-HRMS: m/z (most abundant peak): calcd.: 7981.92287 [M]$^+$, found: 7981.91367 [M]$^+$.
FTIR: $\tilde{\nu}$ [cm$^{-1}$]: 524.5, 552.5, 561.2, 573.7, 597.8, 624.8, 660.5, 746.3, 765.6, 799.4, 955.6 (s, E-C=C), 1047.2, 1094.4 (s, C-O-C) 1258.3, 1340.3, 1374.0, 1429.0, 1455.0, 1506.1, 1575.6 (m, aromat. C=C), 1750.1 (s, C=O), 2849.3, 2918.7 (s, CH$_3$).

Melting point: Decomposition $> 300$ °C.

Elemental analysis (%) for C$_{536}$H$_{412}$N$_{12}$O$_{56}$Zn calcd.: C 80.65; H, 5.20; N, 2.11 found: C 77.88, H 5.22, N 2.42. see comment [A] page 19

[A]
The elemental analysis of compounds 1b and 2b show satisfying results regarding the values of H and N. However, the values for C are too low for the two target molecules. This is a well-known problem, that lots of phthalocyanines show lower values for C due to incomplete combustion.$^{3,4,5}$

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3 Y. Takagi, K. Ohta, S. Shimosugi, T. Fujii, E. Itoh, J. Mater. Chem., 2012, 22, 14418–14425.
4 Z. Zao, T. Nyokong, M. D. Maree, Dalton Trans. 2005, 3732–3737.
5 T. Kamei, T. Kato, E. Itoh, K. Ohta, J. Porphyrins Phthalocyanines 2012; 16: 1261–1275.
4) NMR spectra of 1b and 2b

Figure S1. $^1$H NMR spectrum (THF-$d_8$, 400 MHz) of 1b between 6.7 ppm and 9.3 ppm.

The best resolution of the aromatic region of compound 1b could be achieved in THF-$d_8$ (Figure S1). The positions and integrals of the signals attributed to the olefinic and aromatic hydrogens are in agreement with the structure. Especially in the aromatic region, phthalocyanines show very broad peaks, due to aggregation and the mixture of different regioisomers, what complicates evaluation of the spectra.\textsuperscript{6,7,8} The assignment of the hydrogen signals to the aromatic and olefinic protons of 1b is supported by 2D-NMR spectroscopy.

\textsuperscript{6} M. Sommerauer, C. Rager, M. Hanack, \textit{J. Am. Chem. Soc.} \textbf{1996}, \textit{118}, 10085-10093.

\textsuperscript{7} B. Görlach, M. Drachtler, T. Glaser, K. Albert, M. Hanack, \textit{Chem. Eur. J.} \textbf{2001}, \textit{7}, No. 11, 2459-2465.

\textsuperscript{8} M. Ince, F. Cardinali, J-H Yum, M. V. Martinez-Diaz, M. K. Nazeeruddin, M. Grätzel, T. Torres, \textit{Chem. Eur. J.} \textbf{2012}, \textit{18}, 6343 – 6348.
Compound 2b gave even broader signals due to the additional four bulky fullerene units, what makes the evaluation of the spectra more challenging.\textsuperscript{9,10} The resolution of the spectrum could slightly by improved by addition of two drops of pyridine-d\textsubscript{5}.\textsuperscript{11}

Figure S2: \textsuperscript{1}H NMR spectra (DCM, 400 MHz) of 2b without (black) and with (red) two drops of pyridine-d\textsubscript{5}.

Figure S2 shows a comparison of the \textsuperscript{1}H NMR spectra of molecule 2b without (black) and with two drops of pyridine-d\textsubscript{5} (red). The aromatic region without pyridine-d\textsubscript{5} between 6.5 ppm and 9.5 ppm is extreme broad and individual peaks can almost not be observed. After addition of the pyridine-d\textsubscript{5}, separate peaks can much better be identified. Also the signal at 4.6 ppm, which can be attributed to half of the diastereotopic protons of the CH\textsubscript{2} group within the pyrrolidine ring, is more pronounced in the red spectrum.

Moreover, all relevant protons of the fullerene spacer could be identified when they were compared to the spectrum of fullerene 22 (see Figure S3).

\textsuperscript{9} A. Escosura, M. V. Martínez-Díaz, D. Guldi, T Torres, \textit{Journal of the American Chemical Society} \textbf{2006} 128 (12), 4112-4118.
\textsuperscript{10} Y. Geerts, O. Debever, C. Amato, S. Sergeye, \textit{Beilstein J. Org. Chem.} \textbf{2009}, \textit{5}, No. 49.
\textsuperscript{11} M. Bai, R. Song, Y. Zhang, S. Han, X. Song, F. Meng, \textit{Inorg. Chem. Commun.}, \textbf{2013}, \textit{28}, 99–103.
Figure S3: $^1$H NMR spectrum of 2b (red, CD$_2$Cl$_2$ with two drops of pyridine-d$_5$) in comparison with the methyl ester of the fullerene 22 (black, in CDCl$_3$) between 0.9 ppm and 4.9 ppm. The signal at 3.63 ppm in the black spectrum belongs to the methyl group of the ester and is therefore not present in 2b.

Figure S3 shows a comparison of the $^1$H NMR spectra of the fullerene spacer 22 and the target molecule 2b. Proton H4 and one of the protons H1/1’ is superimposed by the signals of the (oligo)ethyleneoxy groups. The $\alpha$-CH$_2$ protons shift to higher ppm values due to the formation of an aromatic esters in the target compound. The assignment of these protons is supported by 2D NMR spectroscopy. However, spectra in Figures S2 and S3 are clearly consistent with the molecular structure and confirm the complete coupling with four fullerene building blocks, which is further supported by the mass spectra (Figure S5B).
Figure S4: $^1$H NMR spectra (CD$_2$Cl$_2$, 400 MHz) of 2b at 295 K between 4.4 ppm and 10.0 ppm.

Figure S4 highlights the aromatic region of compound 2b, which could be best resolved in CD$_2$Cl$_2$ with additional pyridine-d$_5$. It confirms the presence of all aromatic and olefinic protons and is in good agreement with the molecular structure. The broad signal at 4.60 ppm with an integration of four protons can be attributed to half of the diastereotopic protons of the CH$_2$ group, belonging to the pyrrolidine ring (see Figure S3).

The presence of four spacers containing fullerenes was unambiguously confirmed, as Figures S6 and S7 are in good agreement with the molecular structure. Moreover, the successful synthesis is further supported by the mass spectra (Figure S5B).
5) Mass spectra of target compounds

![Graph A](image1)

![Graph B](image2)

**Figure S5.** MALDI-MS spectra of compounds 1b (A) (positive) and 2b (B) (negative). The spectra of 2 clearly shows that four fullerene building blocks are bound to the phthalocyanine since no additional signal at 6982, 5982, 4982 m/z (highlighted with arrows) appears, which would be expected for phthalocyanines with only 3, 2, and only 1 fullerene unit. The additional signal (B) belongs to an unknown decomposition product.
6) DSC measurement of 1b

![DSC trace of 1b](image)

**Figure S6**: DSC heating and cooling cycles of 1b.

DSC trace of 1b between 25 °C and 300 °C do not show any phase transition.

7) Density measurements by the buoyancy method at 22 °C

The density measurement of compound 1b was carried out in mixtures of deionized water and aqueous calcium chloride (40 °wt%) solution. Before dissolving, the calcium chloride was dried at 140 °C under reduced pressure (1 × 10⁻³ mbar). All solvents were degassed by ultrasonication.

The samples were heated to 170 °C and extruded into a thin solid fiber under reduced pressure to avoid inclusion of air. The fiber was cut in small pieces. These samples were put in a vial containing deionized water. Aqueous calcium chloride (40 wt%) solution was added in small portions until the sample started floating. The mixture was allowed to equilibrate between additions. The weight percentage of calcium chloride was determined and the density was calculated according to reference.¹²

Note that this method relies on samples which are free from air inclusions, which cannot be completely guaranteed with the present procedure. For materials with much lower clearing temperatures and high thermal stability in the isotropic liquid, the samples can be prepared by keeping them a long time in the isotropic liquid under vacuum, which is supposed the eliminate all air bubbles.¹³ However in the present case this is not possible since the star-compounds do not melt. Therefore, the present density can be only a minimum value for star 1b.

¹² S. Mao, Z. Duan, J. Chem. Thermodyn 2008, 40, 1046-1063.

¹³ M. Lehmann, M. Jahr, B. Donnio, R. Graf, S. Gemming, I. Popov, Chem. Eur. J. 2008, 14, 3562-3576.
8) Modelling
The modelling of the hexagonal unit cell was performed using the program suite “BIOVIA Materials Studio 2017R2” and the Forcite module with the force field COMPASSII.
For the construction of the unit cell, the set-up for 1b started with the dimers (see Figure 3) placed in the unit cell (a = 63.9 Å, c = 48.1 Å). The dimer was then copied, translated by (48.1/16) Å in c-direction and rotated by (360/16)° about the column axis. After 16 dimers, this procedure generated the complete helix. The cell was geometry optimised first by using the atomic summation method and subsequently applying the Ewald summation method until large negative non-bonding interactions (van der Waals and electrostatic interactions) have been obtained, which support the plausibility of the model (Figure 3).
The models in Figure 5 are used only for the visualization of the click procedure and the size of the molecules and have not been geometry optimized.
9) NMR Spectra

$^1$H NMR (400 MHz) spectrum of 6 in CD$_2$Cl$_2$

$^{13}$C NMR (100 MHz) spectrum of 6 in CD$_2$Cl$_2$
$^1$H NMR (400 MHz) spectrum of 8 in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of 8 in CDCl$_3$
$^1$H NMR (400 MHz) spectrum of 10 in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of 10 in CDCl$_3$
$^1$H NMR (400 MHz) spectrum of 1b in THF-$d_8$

$^{13}$C NMR (151 MHz) spectrum of 1b in THF-$d_8$
$^1$H NMR (400 MHz) spectrum of 12 in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of 12 in CDCl$_3$
$^1$H NMR (400 MHz) spectrum of 13 in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of 13 in CDCl$_3$
$^1$H NMR (400 MHz) spectrum of 14 in CDCl$_3$

$^{13}$C NMR (100 MHz) spectrum of 14 in CDCl$_3$
$^1$H NMR (400 MHz) spectrum of 15 in CD$_2$Cl$_2$

$^{13}$C NMR (100 MHz) spectrum of 15 in CD$_2$Cl$_2$
$^1$H NMR (400 MHz) spectrum of 2b in CD$_2$Cl$_2$ + 2 drops of pyridine-$d_5$

$^{13}$C NMR (151 MHz) spectrum of 2b in CD$_2$Cl$_2$