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A Molecular *Ansa*-Basket: Synthesis of an Inherently Chiral all-Carbon [12](1,6)Pyrenophane

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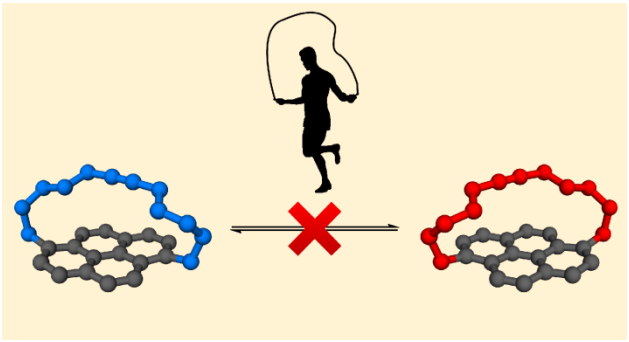


ABSTRACT

The synthesis of an inherently chiral[1] all-carbon C2-symmetric [12](1,6)pyrenophane **1** is reported. The cyclophane **1** was obtained via a ring-closing alkyne metathesis (RCAM) reaction using *Mortreux's* catalyst molybdenum hexacarbonyl and 2-fluorophenol as phenol additive. The *M* and *P* enantiomers of the all-carbon pyrenophane **1** demonstrated to be very stable in their enantiopure form even upon prolonged heating at 200 °C. [12](1,6)pyrenophane-6-yne **1** was fully characterized by high resolution mass spectrometry (HRMS), NMR, UV-Vis and by measured and calculated electronic circular dichroism (ECD) spectroscopy.

INTRODUCTION

Cyclophane chemistry is known for their broad variety of molecular structures and geometries. They are unique molecules consisting of aromatic ring systems, which are bridged by aliphatic chains. Almost no limitations in molecular design and conformational flexibility makes this research topic attractive for structural analysis, physical investigations and for chemical engineering.[2,3] Stereochemistry is one of the many interesting facets of cyclophane chemistry and a considerable number of inherently chiral[1] parent cyclophanes are known.[4–6] The synthesis of inherently chiral[1] and configurationally stable [n]cyclophanes requires an aromatic backbone with enantiotopic faces. Various mononuclear heteroaromatic systems

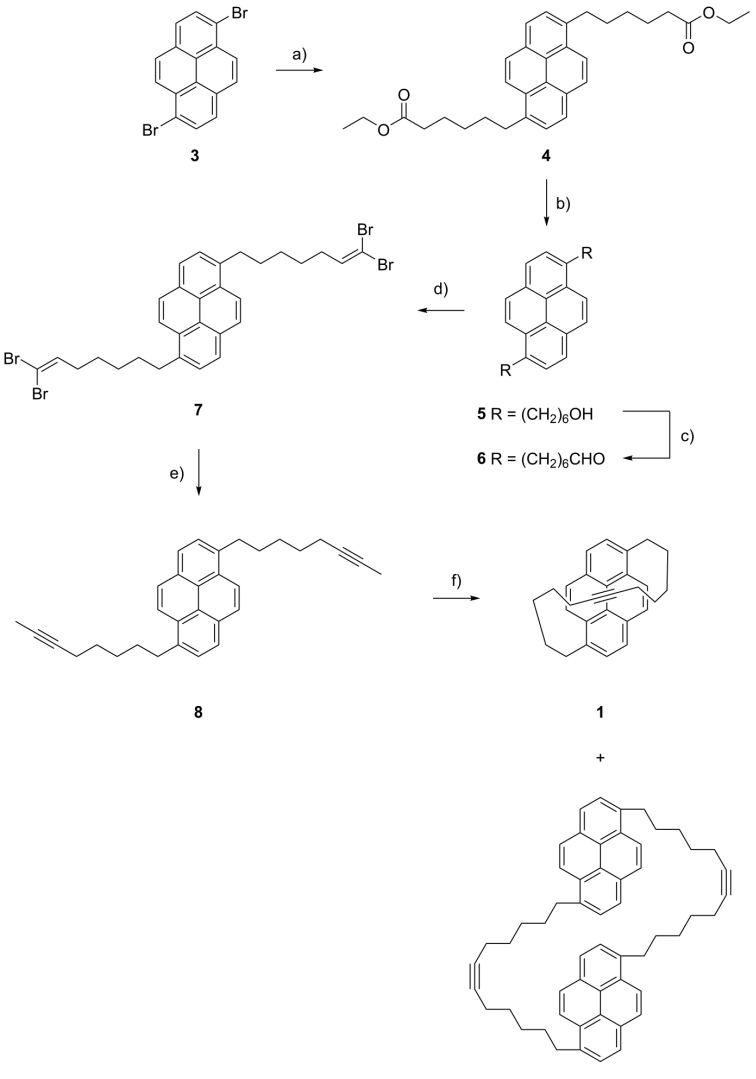
(e.g. pyridin[7]) or larger benzenoid aromatic systems (e.g. naphthalene[8]) with particular bridging motifs are therefore needed for the general synthetic approach. Additionally, the bridge must be short enough to provide configurational stability and with these issues in mind, there are relatively few reports of chiral [n]cyclophane known, which are derived from aromatic backbones larger than benzene.[3,9–12] The backbone "locking" can be achieved by molecular tethering of smaller or larger polyaromatic hydrocarbons (anthracene or perylene) perfectly illustrated by the work of Gidron[13] and Würthner[14]. Pyrene for instance, as an aromatic backbone unit, is a promising system for incorporation into a chiral and configurationally stable [n]cyclophane. The chirality can be introduced via interlocking the 1,6 positions with an oligoalkyl bridge. The enantiomer interconversion of such systems by way of a "skipping rope" process is likely to be difficult, even with reasonably long bridges.[7]

The syntheses and extensive studies of achiral [n](2,7)pyrenophanes[15–18] and [n](2,11)teropyrenophanes[19,20] have been reported by Bodwell and co-workers. They also succeeded to design, synthesize and characterize chiral [n](1,6)pyrenophanes including oxygen atoms in the bridging unit and as well the all-carbon analogue.[21,22] Bodwell's synthetic approach to the chiral all-carbon [n](1,6)pyrenophanes is to generate the pyrene system in a nonplanar conformation using a valence isomerization/dehydrogenation (VID) reaction. Their strategy is to introduce the bridge of the cyclophane in an earlier synthetic step, then macrocyclization followed by pyrene-formation as final step to form highly strained pyrenophanes.

Herein, we report the synthesis of the all-carbon [12](1,6)pyrenophane-6-yne **1** based on an alternative synthetic strategy together with chiroptical and photophysical properties of the target compound. In contrast to Bodwell's approach, our synthetic strategy is to introduce

the bridge of the pyrenophane in the final step via ring-closing alkyne metathesis (RCAM) reaction, providing the pyrenophane in a linear sequence of only six synthetic steps.

RESULTS AND DISCUSSION



Scheme 1: Synthesis of [12](1,6)pyrenophane-6-yne **1**; a.) 1.) Zn (15.0 eq), 2.) I_2 (0.5 eq), 3.) ethyl 6-bromohexanoate (10.0 eq), DMF, 80 °C, 2 d; 4.) $[PdCl_2(PPh_3)_2]$ (10 mol%), DMF, RT, 1 d, **20%**; b.) $LiAlH_4$ (4.2 eq), THF, -45 °C to RT, 15 h, **quant.**; c.) DMP (2.5 eq), DCM, RT, 2 h, **quant**.; d.) 1.) CBr_4 (6.0 eq), 2.) PPh_3 (12.0 eq), DCM, 0 °C, 18 h, **90%**; e.) 1.) *n*-BuLi (5.5 eq), 2.) MeI (20.0 eq), THF, -78 °C, 3 h, **quant.**; f.) $[Mo(CO)_6]$ (10 mol%), 2-fluorophenol (1.0 eq), chlorobenzene, 150 °C, 1-2 h, **4%** for **1** as two enantiomers and **34%** for **2**.

The pyrenophyn **1** was prepared in six synthetic steps starting with a *Negishi* cross-coupling reaction on 1,6-dibromopyrene **3** (Scheme 1). For the *Negishi* cross-coupling reaction the zinc alkyl reagent was obtained using zinc powder and a catalytic amount of iodine in dry DMF. Having the right condition for the transmetalation step, the *Negishi* cross-coupling reaction was only achieved in 20% yield (Scheme 1).[24] According to GC-MS analysis the main side products were the mono substituted ethyl 6'-(6-bromopyren-1-yl)hexanoate and starting material **3** in the ratio of 1:4:5 (1,6-dibromopyrene : 6'-(6-bromopyren-1-yl)hexanoate: diethyl 6',6'-(pyrene-1,6-diyl)dihexanoate). Even after increasing the amount of ethyl 6-bromohexanoate from 5 eq to 10 eq no further conversion was observed. As the following steps developing the precursor **8** for the macrocyclization proceeded in very good to excellent yields, the synthetic strategy was maintained in spite of the limited availability of **4**. Both were achieved in quantitative yields, the reduction of the carboxylic ester **4** to the corresponding alcohol **5** with lithium aluminum hydride, and the conversion of compound **5** to the desired aldehyde **6** using *Dess-Martin* periodinane (DMP).

The conversion from aldehyde **6** to compound **8** was achieved by a reaction sequence known as *Corey-Fuchs* transformation. In a *Wittig* type reaction the aldehyde **6** was converted to the dibromoolefin **7**, which was treated with *n*-BuLi to provide the lithium ethynylate, which was quenched with a large excess of methyl iodide. While the dibromoolefin **7** was isolated in good 90% yield, the methylalkyne **8** was obtained quantitatively.

The methyl end-capping of the terminal alkyne was required for a successful cyclization to **1**. It is literature known that terminal alkynes are incompatible with metathesis catalysts.[24] The key step of the synthesis is the cyclization to pyrenophane **1** based on a RCAM reaction.[25] Due to the proximity of the reaction space of the RCAM reaction to the pyrene unit, small RCAM catalysts without spatially demanding ligands seemed particular promising. Thus, our

attention fell on *Mortreux's* catalyst molybdenum hexacarbonyl and as co-catalyst 2-fluorophenol.[24,26] Different reaction conditions were screened to favor the intramolecular reaction and to avoid the formation of the intermolecular by-product ([12.12](1,6)pyrenophane-6,24-diyne **2**). The best results were obtained with a conventional heating (oil bath) condition using a 2.32 mM solution of **8** in chlorobenzene, 10 mol% of the molybdenum hexacarbonyl catalyst and 1 eq of the co-catalyst 2-fluorophenol refluxing at 150 °C for 1.5 h. After a short plug over Celite® and removing of the solvent under reduced pressure, the cyclophane **1** as well the pyrenophane dimer **2** were isolated by GPC (Dr. Meisch, chloroform, 4 cycles) on a semi-preparative column in 4% yield as two enantiomers, respectively in 34%. The low yield of the formed pyrenophane **1** by the RCAM reaction probably reflects the restricted and limited flexibility of the pyrene core. Forcing the pyrene subunit out of planarity is energetically disfavored and thus, strained and bent pyrenophanes like the ones reported by Bodwell[15–18,21,22] cannot be assembled by our strategy. However, with the spatially modest catalyst $Mo(CO)_6$ the already pretty strained pyrenophane **1** could be obtained, even so in low yields. We initially hypothesized, that the dimer **2** might be a pair of diastereomers, but VT-NMR experiments (between 298 K and 178 K in CD_2Cl_2) showed fast exchange between both possible conformers (see SI).

Due to the planarity of the pyrene backbone unit of intermediate **8**, two enantiomers are formed depending on which side the metathesis is taking place (enantiotopic faces). The racemic mixture of **1** was successfully baseline separated into their enantiomers **1a** and **1b** by HPLC using a chiral stationary phase (Chiracel OD-H, 1 mL min^{-1}, 98:2 *n*-hexane:*i*-PrOH, 25 °C) (see SI Figure S1). For each pyrenophane the corresponding *M* and *P* enantiomer were isolated in high enantiomeric purities (> 99% ee). Further evidence, that the two isolated fractions were optical isomers, was confirmed by ECD measurements (Figure 1a). We recorded

ECD spectra for each isomer, **1a** and **1b**, in *n*-hexane:*i*-PrOH (98:2) at 25 °C after HPLC separation. Complementary Cotton effects were observed for each isomer (**1a**,**b**: λ = 382 nm, 352 nm, 334 nm, 280 nm, 271 nm and 235 nm). To study the racemization process by HPLC using the chiral stationary phase, we isolated pure fractions of pyrenophane **1a** and **1b**. The samples were dissolved in 1-octadecene and exposed to 150 °C, 200 °C and 250 °C (see SI). No enantiomerization of the enantipure pyrenophane was observed, but slow decomposition of the compound at 250 °C (see SI Figure S5). Thus the experimental data not only confirm thermal stability up to 200 °C, but also that the decomposition temperature is reached prior to the enantiomerization temperature of the pyrenophane.

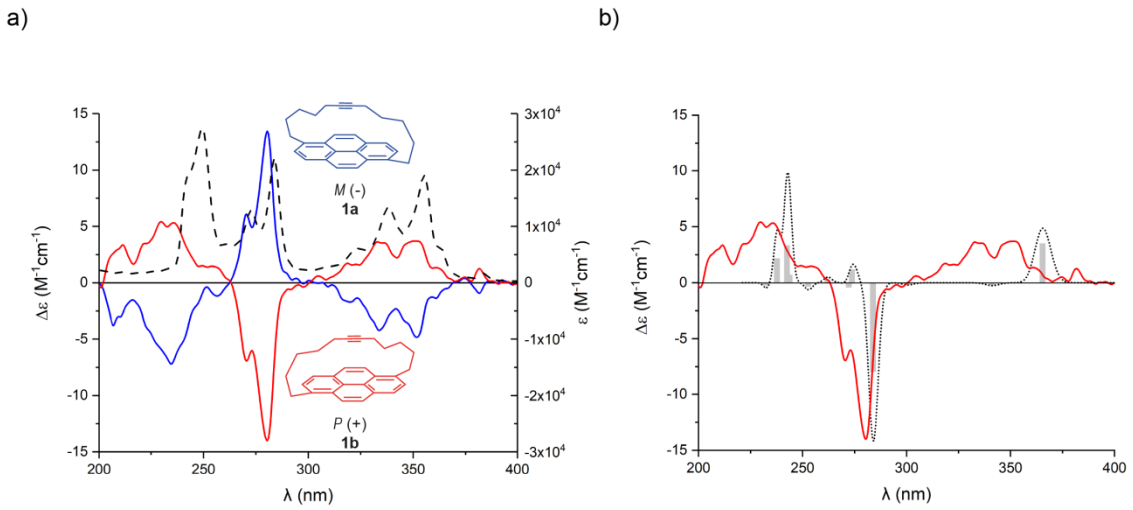


Figure 1: a) Electronic circular dichroism spectrum of the enantiomeric pair of **1** (*n*-hexane:*i*-PrOH (98:2), 25 °C); **1a** in blue, **1b** in red and UV-Vis spectrum of the racemic mixture **1** (chloroform, 25 °C) in dashed lines. b) Calculated ECD spectrum of **1b** with B3LYP/6-311+G(2d,p) basis set. The calculated spectrum is based on the geometry-optimized structure. Red solid line: Experimental spectra, black dots: Calculated spectra, grey bars: Calculated transitions with scaled intensities.

Several attempts to crystallize the racemic mixture as well as the individual enantiomers of cyclophane **1** were not successful. However, the absolute configuration was assigned by comparison of the calculated and measured ECD spectra (Figure 1b). For the

calculation, the THF-solvated geometry optimized structure was used as starting point with B3LYP/6-311+G(2d,p) basis set. Time-dependent calculations (B3LYP/6-311+G(2d,p)) were performed to obtain the simulated ECD spectra and the impact of conformational change and level of theory were investigated for possible impact on calculated signal positions and intensities (see SI for details). A good qualitative agreement was observed between experimentally recorded and calculated ECD spectra for both enantiomers, with the predominantly positive regions around 200 – 250 nm, strong negative signal around 280 nm and broad positive region around 310 – 360 nm all corresponding to similar features in the calculated spectrum (Figure 1b). This allowed the final assignment of **1a** as the *M* helices and **1b** as the *P* helices. Note that signals around 200 – 250 nm were found to be sensitive to level of theory and molecular conformation used in the calculations (see SI), accounting for lack of quantitative agreement in this region. As potential reason for the absence of splitting in the signal around 350 nm we hypothesize the lack of explicit solvent molecules in the calculations.

The signals of the ^{1}H-NMR of [12](1,6)pyrenophane derivative **1** were assigned by using standard 1D and 2D NOE experiments (see SI Table S1). The protons of the alkyl chain are diastereotopic, due to the rigid conformation of **1**. The most pronounced effect is observed for the bridge protons (see SI Table S1: H_γ = 0.88, 0.84; H_δ = 0.32, -0.40 and H_ε = 0.99, 1.22 ppm), which lie across the face of the pyrene backbone. The distinct high field shift of these protons is the result of the deeper orientation into the shielding zone of the pyrene nucleus. This can be explained and visualized by the anisotropic effect using the aromatic ring current model.[27]

The UV-Vis absorption spectra of **1** bears a resemblance to that of pyrene itself with bands λ_{max} (ε, M^{-1} cm^{-1}) at 383 (1.8 x 10^3), 354 (1.9 x 10^4), 337 (1.3 x 10^4), 322 (6.1 x 10^3), 283 (2.2 x 10^4), 272 (1.3 x 10^4) nm (Figure 1a, dashed lines). In the short wavelength region of the

spectrum (313 to 355 nm) structured absorption bands are observed, which are related to the individual absorptions of the pyrene unit of compound **1**.

The fluorescence spectra of pyrenophane **1** (Figure 2) exhibit structured fluorescence emissions around 375 and 430 nm. The fluorescence quantum yield (ϕ_f) for **1** is 0.68 and the fluorescence lifetime (τ_f) is 80.6 ns in *n*-hexane. This compares to ϕ_f = 0.64 and τ_f = 480 ns for pyrene.[28] According to the studies of Konishi and co-workers the alkyl chain enhance the quantum yield ϕ_f of the pyrene unit through the σ-π conjugation.[29]

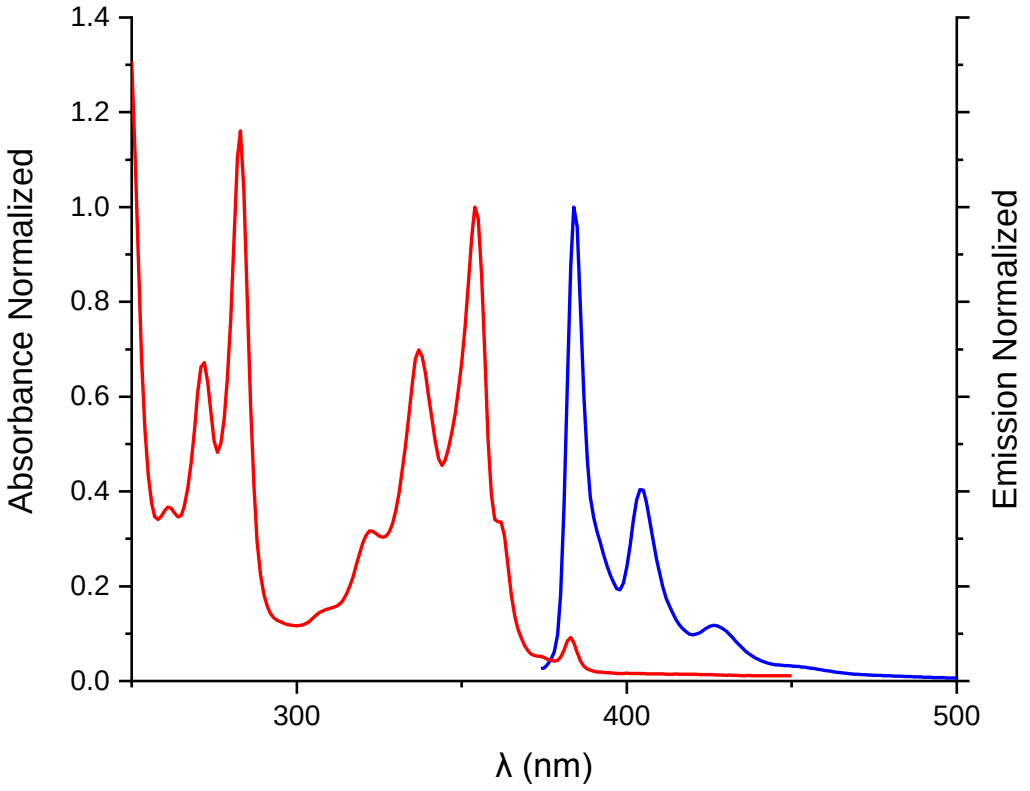


Figure 2: Normalized absorption (red) and emission spectra (blue) for pyrenophane **1** in $CHCl_3$ at 298 K. Excitation wavelength: 354 nm for **1**.

CONCLUSION

In summary, the design and the synthesis of all-carbon [12](1,6)pyrenophane **1** with inherent chirality[1] is described. The chiroptical properties as well as the molecular structure was confirmed by 1D and 2D NMR studies (^{1}H-NMR, ^{13}C{^{1}H} NMR, HMQC, HMBC, NOESY and COSY), mass spectrometry (MALDI-TOF, DART, ESI and GC-MS), UV-Vis, ECD and fluorescence spectroscopy. We succeeded to baseline separate the two stable enantiomers in high enantiomeric purities (> 99% ee) from the racemic product by HPLC using a chiral-packed column (Chiracel OD-H). Finally, the absolute configuration was determined by comparison of the experimental and calculated ECD spectra using TD-DFT calculation.

As a future project, we consider to further functionalize the ethynyl bridged cyclophane **1** towards a charge-transfer (CT) pyrenophane. CT complexes are of special interest in the development of molecular wires, superconductors and new conductive materials.

EXPERIMENTAL SECTION

General Methods: All chemicals were directly used for the synthesis without further purification, unless stated differently. All reactions were carried out in an oil bath and with a heating plate. Solvents for photophysical measurements were HPLC grade. Dry solvents were used as crown cap and purchased from *Acros Organics* and *Sigma-Aldrich*. NMR solvents were obtained from *Cambridge Isotope Laboratories, Inc.* (Andover, MA, USA). ^{1}H-NMR and ^{13}C{^{1}H} NMR were recorded on *Bruker Avance III-NMR* instruments operating at 400 or at 600 MHz proton frequencies. Both instruments were equipped with BBFO direct observe probe heads with shielded z-gradients. The VT-NMR experiments were performed at 600 MHz using an indirect BBI z-gradient probe. The temperature was calibrated using a methanol standard showing accuracy within +/- 0.2 K. Chemical shifts (δ) are reported in parts per million (ppm)

relative to the residual solvent peak. Coupling constants (*J*) are given in Hertz (Hz). DART-MS was measured on a IonSense DART-SVP100 (He, 450 °C) connected to a Shimadzu LC-2020. Gas Chromatography (GC-MS) was performed on a *Shimadzu* GCMS-QP2010 SE gas chromatograph system, with a ZB-5HT inferno column (30 m x 0.25 mm x 0.25 mm), at 1 mL/min He-flow rate (split = 20:1) with a *Shimadzu* mass detector (EI 70 eV) was used. For high resolution mass spectra (HRMS) a HR-ESI-ToF-MS measurement on a *maXis™ 4G* instrument from *Bruker* was performed. High-resolution electron ionization mass spectrometry was performed on a *Thermo DFS* (*ThermoFisher Scientific*, Bremen, Germany) double-focusing magnetic sector mass spectrometer (geometry BE). Mass spectra were measured in electron impact (EI) mode at 45 eV, with solid probe inlet, a source temperature of 200 °C, an acceleration voltage of 5 kV, and a resolution of 10'000. The instrument was scanned between e.g. *m/z* 300 und 350 at scan rate of 100-200 s / decade in the electric scan mode. Perfluorokerosene (PFK, Fluorochem, Derbyshire, UK) served for calibration. Column chromatography was performed with SiliaFlash® P60 from *SILICYCLE* with a particle size of 40-63 µm (230-400 mesh) and for TLC *Silica gel 60 F_{254}* glass plates with a thickness of 0.25 mm from *Merck* were used. The detection was observed with a UV-lamp at 254 or 366 nm. Gel Permeation Chromatography (GPC) was performed on a Shimadzu Prominence System with PSS SDV preparative columns from PSS (2 columns in series: 600 mm x 20.0 mm, 5 µm particles, linear porosity "S", operating ranges: 100 – 100 000 g.mol-1) using chloroform as eluent. For HPLC a Shimadzu LC-20AB, LC-20AD, LC-20AP and a LC-20AT HPLC, respectively, was used equipped with a diode-array UV/Vis detector (SPD-M20A VP from Shimadzu, λ = 200-600 nm) and a column oven Shimadzu CTO-20AC. The used column for chiral separation a Daicel OD-H, 5 µm, 4.6 x 250 mm; Daicel Chemical Industries Ltd. CD measurements were performed on a JASCO J-1500 CD Spectrophotometer in *n*-hexane:*i*-PrOH 98:2 mixture at 25

°C in a 1115F-QS Hellma cuvettes (10 mm light path) directly after the chiral HPLC separation. UV/Vis absorption spectra were recorded on a Jasco V-770 Spectrophotometer using optical 1115F-QS Hellma cuvettes (10 mm light path). The wavelength was measured in nm. All solutions were prepared and measured under air saturated conditions if not otherwise stated. Quantum yields (chloroform) were measured using a Hamamatsu absolute photoluminescence quantum yield spectrometer C11347 Quantaurus-QY. Emission lifetimes were measured with a Hamamatsu Compact Fluorescence lifetime Spectrometer C11367 Quantaurus-Tau, using an LED light source with λ_{exc} = 340 nm. Quantum yield and fluorescence life time measurements were performed under argon saturated conditions. The excitation wavelength was 340 nm and the emission wavelength was 385 nm. The concentration of the sample in chloroform was 7.4 x 10^{-7} M and in *n*-hexane 3.8 x 10^{-6} M for pyrenophane **1**.

Diethyl 6',6'-(pyrene-1,6-diyl)dihexanoate (4). In a dry 250 mL Schlenk tube under argon flow zinc dust (8.20 g, 125 mmol, 15.0 eq), I_2 (1.00 g, 4.20 mmol, 0.50 eq) and DMF (80 mL) were added. The mixture was stirred at RT until the red color of I_2 disappeared. The freshly distilled (60 °C, 2.6^{-1} mbar) ethyl 6-bromohexanoate (14.8 mL, 83.3 mmol, 10.0 eq) was added and the reaction mixture was stirred at 80 °C overnight. (The completion of the zinc insertion reaction was indicated by GC analysis of the hydrolyzed reaction mixture.) The mixture was cooled to RT and then 1,6-dibromopyrene (**3**, 3.00 g, 8.30 mmol, 1.00 eq) and [$PdCl_2(PPh_3)_2$] (600 mg, 800 μmol, 10 mol%) were added successively. The reaction mixture was stirred over night at RT and then it was quenched with H_2O (60 mL). The remaining zinc dust was filtered off and washed with Et_2O. The aqueous layer was extracted with diethyl ether (3 x 100 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated. The crude residue was purified by flash column chromatography on silica gel (Gradient, cyclohexane to cyclohexane:ethyl acetate (30:1) to (5:1)) to isolate the product. After recrystallization in *n*-

hexane the product (**4**, 800 mg, 1.65 mmol, 20%) was isolated as white crystals: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 8.20 (d, *J* = 9.2 Hz, 2H), 8.11 – 8.02 (m, 4H), 7.84 (d, *J* = 7.8 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 4H), 3.37 – 3.30 (m, 4H), 2.31 (t, *J* = 7.5 Hz, 4H), 1.88 (tt, *J* = 9.7, 6.8 Hz, 4H), 1.78 – 1.67 (m, 4H), 1.57 – 1.47 (m, 4H), 1.24 (t, *J* = 7.1 Hz, 6H) ppm; ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 25 °C): δ = 173.9, 136.8, 129.7, 129.00, 127.5, 127.3, 125.6, 124.6, 122.7, 60.4, 34.5, 33.7, 31.6, 29.4, 25.1, 14.4 ppm; GC-MS (EI +, 70 eV): m/z (%) = 486 (41), 357 (50), 241 (42), 228 (100); DART-MS (450 °C, +): *m/z* (%) = 505 (31), 504 (100) $[M+NH_4]^+$, 488 (15), 487 (46) $[M+H]^+$, 486 (8); HRMS (ESI-TOF): m/z calc. for $C_{32}H_{38}NaO_4$ 509.2662 $[M+Na]^+$; found 509.2662.

6',6'-(Pyrene-1,6-diyl)bis(hexan-1'-ol) (5). To a solution of diethyl 6',6'-(pyrene-1,6-diyl)dihexanoate (**4**, 50.0 mg, 100 μmol, 1.00 eq) in dry THF (10 mL) at -45 °C was added $LiAlH_4$ (1.0 M in THF, 430 μL, 430 μmol, 4.20 eq). The resulting mixture was stirred at -45 °C for 1 h, warmed to -10 °C for 1 h, then slowly warmed to RT and stirred for 15 h at this temperature. The reaction mixture was cooled to 4 °C and treated sequentially with H_2O (2 mL), 10% aq. sodium hydroxide (2 mL), and with H_2O (4 mL) again. Diethyl ether (10 mL) was then added and the solution was allowed to stir for 90 min. The organic layer was separated and the aq. phase was extracted with diethyl ether (3 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated in *vacuo* to give the desired product (**5**, 41.0 mg, 100 μmol, quant.) as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.20 (d, *J* = 9.3 Hz, 2H), 8.12 – 8.01 (m, 4H), 7.84 (d, *J* = 7.8 Hz, 2H), 3.64 (t, *J* = 6.6 Hz, 4H), 3.40 – 3.24 (m, 4H), 1.92 – 1.80 (m, 4H), 1.66 – 1.37 (m, 15H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ = 137.0, 129.6, 129.0, 127.4, 127.3, 125.6, 124.6, 122.7, 63.1, 33.8, 32.9, 32.0, 29.7, 25.8 ppm; MALDI-TOF (positive ion mode): m/z (%) = 402 (100) ; DART-MS (450 °C, +): *m/z* (%) = 403 (100) $[M+H]^+$, 404 (26); HRMS (ESI-TOF): m/z calc. for $C_{28}H_{34}NaO_2$ 425.2451 $[M+Na]^+$; found 425.2451.

6',6'-(Pyrene-1,6-diyl)dihexanal (6). In an oven dried, argon flushed two-necked flask (50 mL) Dess-Martin periodiane (342 mg, 780 μmol, 3.50 eq) was dissolved in DCM (10 mL). To the mixture 6',6'-(pyrene-1,6-diyl)bis(hexan-1'-ol) (**5**, 90.0 mg, 224 μmol, 1.00 eq) dissolved in DCM (5 mL) was added and the reaction mixture was stirred at RT for 1.5 h. To the reaction mixture DCM (10 mL) was added additional and the solution was carefully quenched with a 1:1 mixture of sat. aq. $NaHCO_3$ (10 mL) and sat. aq. $Na_2S_2O_3$ (10 mL) before washing with a 1:1 mixture of sat. aq. $NaHCO_3$ (10 mL) and sat. aq. $Na_2S_2O_3$ (10 mL), followed by brine (20 mL). The organic layer was dried over Na_2SO_4, filtered and after removal of the solvent under reduced pressure and purification by flash column chromatography on silica gel (Cyclohexane:Ethyl acetate (5:1) the product (**6**, 89.3 mg, 224 μmol, quant.) was isolated as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 9.76 (t, *J* = 1.7 Hz, 2H), 8.20 (d, *J* = 9.2 Hz, 2H), 8.07 (dd, *J* = 13.5, 8.5 Hz, 4H), 7.84 (d, *J* = 7.7 Hz, 2H), 3.40 – 3.29 (m, 4H), 2.44 (td, *J* = 7.3, 1.8 Hz, 4H), 1.93 – 1.82 (m, 4H), 1.72 (p, *J* = 7.4 Hz, 4H), 1.56 – 1.47 (m, 5H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ = 202.8, 136.7, 129.7, 129.0, 127.5, 127.4, 125.6, 124.6, 122.6, 44.0, 33.6, 31.7, 29.4, 22.2 ppm; GC-MS (EI +, 70 eV): m/z (%) = 396 (60), 313 (100), 228 (50); DART-MS (450 °C, +): *m/z* (%) = 418 (6), 417 (28), 416 (100) $[M+NH_4]^+$, 400 (12), 399 (46) $[M+H]^+$; HRMS (ESI-TOF): m/z calc. for $C_{28}H_{30}NaO_2$ 421.2138 $[M+Na]^+$; found 421.2138; calc. for $C_{28}H_{30}KO_2$ 437.1877 $[M+K]^+$; found 437.1877.

1,6-Bis(7,7-dibromohept-6-en-1-yl)pyrene (7). An oven dried, argon flushed two-neck round bottomed flask (100 mL) was charged with a mixture of CBr_4 (794 mg, 2.37 mmol, 6.00 eq) and PPh_3 (1.26 g, 4.74 mmol, 12.0 eq) in 30 mL of dry DCM and was stirred at 0 °C for 1 h. Then a solution of 6',6'-(pyrene-1,6-diyl)dihexanal (**6**, 309 mg, 775 μmol, 1.00 eq) in 20 ml of dry DCM was added drop wise. The mixture was stirred at 0 °C for 1 h. After the removal of solvent under reduced pressure, the residue was purified by flash chromatography on a plug of silica

gel using DCM as eluent. The product (**7**, 494 mg, 696 μmol, 90%) could be isolated as yellow solid: ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ = 8.23 (d, *J* = 9.2 Hz, 2H), 8.16 – 8.03 (m, 4H), 7.87 (d, *J* = 7.8 Hz, 2H), 6.43 (t, *J* = 7.3 Hz, 2H), 3.46 – 3.24 (m, 4H), 2.12 (tdd, *J* = 7.1, 4.7, 2.1 Hz, 4H), 1.86 (dddd, *J* = 11.9, 7.2, 4.7, 2.4 Hz, 4H), 1.52 (p, *J* = 3.7 Hz, 8H); ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 25 °C): δ = 139.7, 137.5, 130.1, 129.4, 127.8, 127.8, 125.9, 125.0, 123.1, 88.8, 34.1, 33.5, 32.1, 29.7, 28.3; DART-MS (450 °C, +): *m/z* (%) = 728 (24) $[M+NH_4]^+$, 727 (27), 726 (18), 725 (35), 724 (15), 723 (25), 721 (8), 715 (10), 714 (19), 713 (52), 712 (50), 711 (92), 710 (24) $[M+H]^+$, 709 (100) $[M]^+$, 708 (12), 707 (33); HRMS (MALDI-TOF): m/z calc. for $C_{30}H_{30}Br_4^+$ 705.90810 $[M]^+$; found 705.90831.

1,6-Di(oct-6'-yn-1'-yl)pyrene (8). To a solution of 1,6-bis(7,7-dibromohept-6-en-1-yl)pyrene (**7**, 122 mg, 170 μmol, 1.00 eq) dissolved in anhydrous THF (10 mL) was added *n*-BuLi (1.6 M in *n*-hexane, 600 μL, 950 μmol, 5.50 eq) at -78 °C. The solution was stirred at -78 °C for 3 h. At the same temperature the mixture was quenched with a solution of CH_3I (200 μL, 3.40 mmol, 20.0 eq) in THF (5 mL) and the reaction mixture was left strring for 1 h. The reaction was quenched with a 10% NaOH (10 mL) aqueous solution. The mixture was stirred for an additional 30 min and the aqueous layer was extracted with ethyl acetate (3 x 20 mL). The combined organic extracts were washed with brine, and dried over Na_2SO_4. After filtration and removal of the solvent at reduced pressure, the residue was purified by column chromatography on silica gel using cyclohexane/ethyl acetate = 30:1 to give the product (**8**, 71.1 mg, 170 μmol, quant.) as a yellow solid: ^{1}H-NMR (400 MHz, CD_2Cl_2, 25 °C): δ = 8.23 (d, *J* = 9.2 Hz, 2H), 8.08 (dd, *J* = 14.4, 8.5 Hz, 4H), 7.87 (d, *J* = 7.7 Hz, 2H), 3.44 – 3.27 (m, 4H), 2.15 (ddt, *J* = 6.7, 4.1, 2.5 Hz, 4H), 1.86 (dq, *J* = 9.7, 6.8, 4.9 Hz, 5H), 1.76 (t, *J* = 2.5 Hz, 6H), 1.58 (p, *J* = 3.6 Hz, 8H) ppm; ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 25 °C): δ = 137.6, 130.1, 129.4, 127.8, 127.7, 125.9, 125.0, 123.1, 79.6, 75.8, 34.1, 32.0, 29.7, 29.6, 19.2, 3.7 ppm; GC-MS (EI +, 70

eV): m/z (%) = 418 (95), 323 (100), 228 (50); DART-MS (450 °C, +): *m/z* (%) = 437 (9), 436 (33) $[M+NH_4]^+$, 420 (31), 419 (100) $[M+H]^+$; HRMS (MALDI-TOF): m/z calc. for $C_{32}H_{34}^+$ 418.26605 $[M]^+$; found 418.26625.

[12](1,6)Pyrenophane-6-yne (1) and [12.12](1,6)pyrenophane-6,24-diyne 2. A 100 mL two-necked round bottom flask equipped with reflux condenser was charged with 1,6-di(oct-6'-yn-1'-yl)pyrene (**7**, 68.0 mg, 160 μmol, 1.00 eq), $[Mo(CO)_6]$ (4.3 mg, 0.02 mmol, 10 mol%), 2-fluorophenol (14.9 μL, 160 μmol, 1.00 eq) and dry chlorobenzene (70 mL). The reaction mixture was left stirring in a preheated oil bath for 1.5 h at 150 °C. The solution was filtrated over a plug of Celite®, the solvent was evaporated and the residue was purified by GPC (chloroform). The product **1** (2.30 mg, 6 μmol, 4%) was isolated as viscous oil and the pyrenophane dimer **2** (19.7 mg, 27 μmol, 34%) as yellow solid: ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C) (signals attributable to **1**): δ = 8.27 (d, *J* = 9.1 Hz, 2H), 8.11 – 8.02 (m, 4H), 7.81 (d, *J* = 7.7 Hz, 2H), 3.84 (ddd, *J* = 13.1, 7.8, 4.5 Hz, 2H), 3.07 (ddd, *J* = 13.4, 8.4, 4.6 Hz, 2H), 1.97 (tdd, *J* = 13.4, 8.3, 4.9 Hz, 2H), 1.60 – 1.54 (m, 2H), 1.24 – 1.17 (m, 2H), 0.98 (dt, *J* = 16.0, 7.9 Hz, 2H), 0.94 – 0.78 (m, 4H), 0.31 (tdd, *J* = 14.6, 9.4, 5.7 Hz, 2H), -0.33 – -0.47 (m, 2H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 25 °C): δ = 136.7, 129.4, 129.3, 127.5, 126.6, 125.5, 124.4, 122.9, 78.2, 33.2, 29.2, 28.2, 26.9, 17.8 ppm; GC-MS (EI +, 70 eV): m/z (%) = 364 (100), 241 (23), 228 (90); MALDI-TOF (positive ion mode): m/z (%) = 366 (1), 365 (28), 364 (100) ; DART-MS (450 °C, +): *m/z* (%) = 365 (100) $[M+H]^+$, 366 (20); HRMS (MALDI-TOF): m/z calc. for $C_{28}H_{28}^+$ 364.21910 $[M]^+$; found 364.2186: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) (signals attributable to **2**): δ = 8.00 (d, *J* = 9.2 Hz, 4H), 7.83 – 7.74 (m, 8H), 7.61 (d, *J* = 7.8 Hz, 4H), 3.13 (t, *J* = 7.6 Hz, 8H), 2.17 – 2.07 (m, 10H), 1.76 (p, *J* = 7.3 Hz, 9H), 1.48 (td, *J* = 7.1, 5.3, 3.1 Hz, 15H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ = 136.6, 129.5, 128.9, 127.3, 127.0, 125.5, 124.4, 122.5, 80.6, 33.4, 31.0, 28.7, 28.6, 18.7 ppm; MALDI-TOF (positive ion mode): m/z (%) = 730.895 (6), 729.907 (48), 728.827 (100) ;

DART-MS (550 °C, +): *m/z* (%) = 729 (100) $[M+H]^+$; HRMS (MALDI-TOF): m/z calc. for $C_{56}H_{56}$ 728.4382 [M]; found 728.4376.

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ASSOCIATED CONTENT

Supporting Information

^{1}H NMR, $^{13}C\{^1H\}$ NMR and Mass spectra for compounds **1**-**8** and DNMR spectrum for **2**. HPLC chromatogram and CD spectra of the corresponding *M* and *P* of **1**. Computational data, geometry-optimized structure of **1** and energy levels of molecular orbitals of **1a** and **1b**.

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