Synthesis and Liquid Crystalline Self-Assembly of Concave Diindoles with a Hydropentalene Core

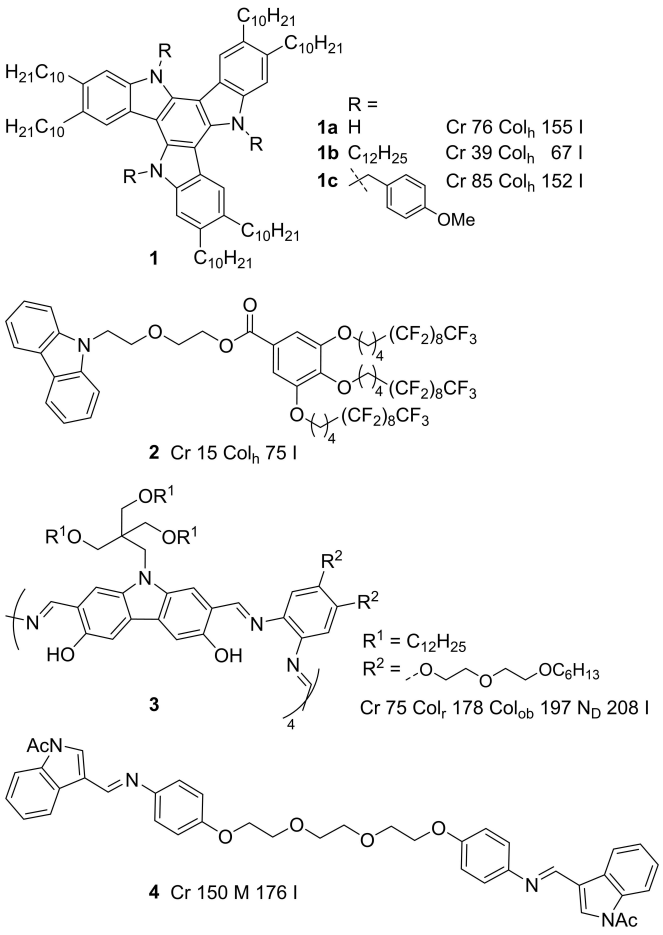
Andrea Bühlmeyer,[a] Philipp Ehni,[a] Dustin Ullmann,[a] Wolfgang Frey,[a] Angelika Baro,[a] and Sabine Laschat*[a]

Fischer indole reaction of Weiss diketone with 4-bromophenylhydrazine provided the 2,8-dibromo-hexahydropentaleno[2,1-*b*:5,4-*b*']diindole key intermediate, which was converted to the target compounds by *N*-protection/Suzuki cross-coupling. Variation of protecting groups, mesogenic units, and their alkoxy substitution gave calamitic diindole mesogens. Both *N*-protection and alkoxy chain influenced the mesomorphic properties of phenyl diindoles. Among the differently *N*-protected derivatives only ethylcarbamate-protected ones formed enantiotropic mesophases. Mesophase range and type were controlled by the chain lengths: chains ≤ C12 gave nematic (N) phases, diindoles with side chains ≥ C14 formed additional lower temperature smectic (SmA) phases. Irrespective of the chain lengths 4′-alkyloxybiphenyl diindoles formed N and SmA phases upon first heating but tended to decomposition below their clearing points. X-ray crystal structure analysis of bis(4′-decyloxy) biphenyl diindole reveals that in the solid-state the folding angle of the hydropentalene core caused an almost perpendicular orientation of the two indole/biphenyl parts with respect to each other.

Introduction

Indole derivatives are key building blocks for organic materials, natural products, pharmaceuticals, agrochemicals, biopolymers, and synthetic functional polymers. With respect to material science their electron-rich heteroaromatic π-system, fluorescence, hole conducting properties, and versatile functionalization make them ideal candidates for dye-sensitized solar cells, organic photovoltaics, organic light-emitting diodes, and organic field-effect transistors.[1] Regarding liquid crystalline indole materials, most work has been carried out on indole-containing discotic and dendrimeric liquid crystals. Typical examples are the star-shaped triindoles **1** developed by Omenat,[2] taper-shaped dendrons **2** reported by Percec,[3] and shape-persistent macrocycles **3** published by Tanaka (Scheme 1).[4]

In the majority of these cases, carbazole moieties were used rather than the parent indoles.[5,6] Calamitic indoles (or carbazoles) were only rarely explored. Marin disclosed a dimer **4**, where the two *N*-acetylindole moieties are connected via a flexible triethylene glycol spacer.[7] However, the phase type could not be assigned due to the lack of XRD data. More



Scheme 1. Some selected liquid crystalline indole materials from the literature.

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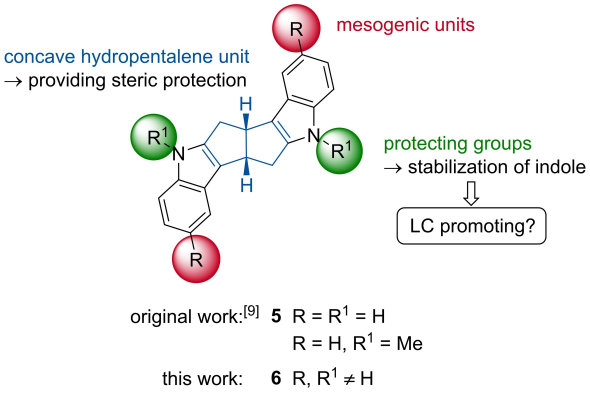
recently, a nematic carbazole-containing rigid oligomer was reported by O'Neill.[8]

This lack of information on liquid crystalline indole derivatives might be due to the pronounced tendency of indoles towards oxidation and subsequent polymerization.[1f] In order to avoid such complications and to tailor mesomorphic properties by suitable functionalization, we chose the hexacyclic diindole unit on the basis of unsubstituted compound **5**, which was originally synthesized by Cook to obtain a fully conjugated pentaleno[2,1-*b*:5,4-*b'*]diindole scaffold[9] (Scheme 2).[10]

We aimed at compound **6** carrying mesogenic units. The protecting groups at the indole nitrogen were intended to stabilize the indole against oxidative decomposition and to promote mesophase formation. Furthermore, the *concave* saturated hydropentalene spacer unit[11] sterically shields the indole moiety against sequential oxidation/polymerization reactions. In the current manuscript, we report the successful realization of this design concept.

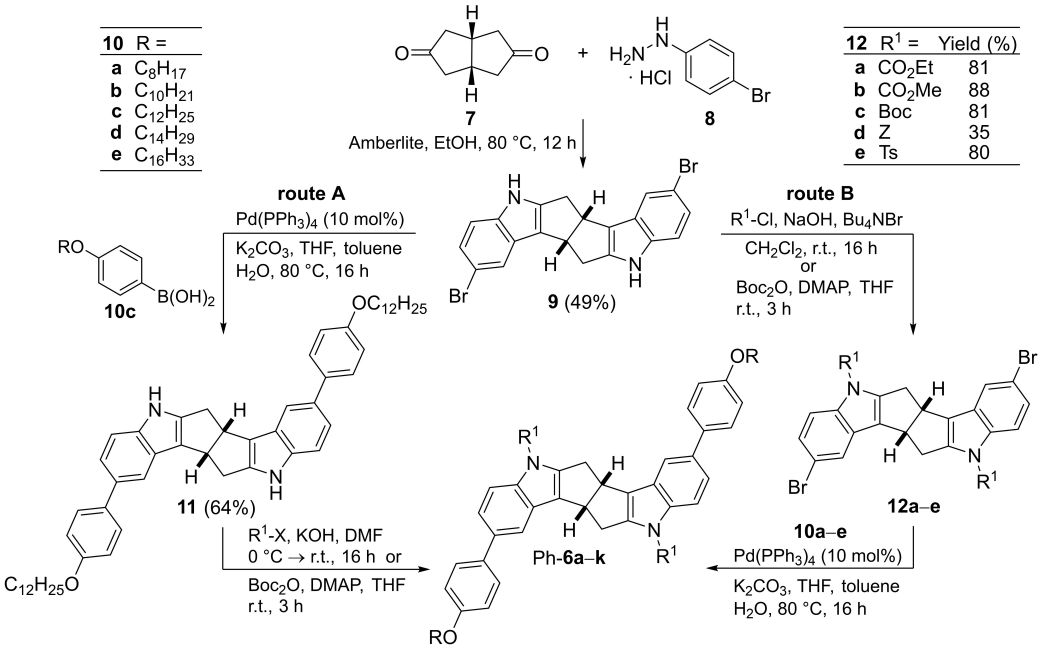


Scheme 2. Envisaged hexacyclic diindole moiety **6**.

Results and Discussion

Synthesis of Diindoles

The synthesis of diindoles **6** commenced with a twofold Fischer indole synthesis of Weiss diketone **7**[12] with 4-bromophenylhydrazine hydrochloride **8** (Scheme 3). The initial protocol by Kotha[13] utilizing thionyl chloride in EtOH at 70 °C for 24 h provided dibromodiindole **9** in only 29 %, and thus, other acids and conditions were tested (Table S1). According to a modified Fischer indole synthesis by Chandrasekhar[14] using the solid acid Amberlite® IR120, a cation exchange resin, Weiss diketone **7** and bromophenylhydrazine **8** finally were reacted in refluxing EtOH for 12 h, then the resin was filtered off and derivative **9** was isolated in 49 % after workup (Scheme 3). It should be emphasized that a two-step protocol towards **9** via Fischer indole synthesis using phenylhydrazine, followed by bromination of the resulting diindole was not amenable (Table S2, Supporting Information), as was previously reported for the bromination of cyclopenta[*b*]indoles with standard bromination reagents.[15]



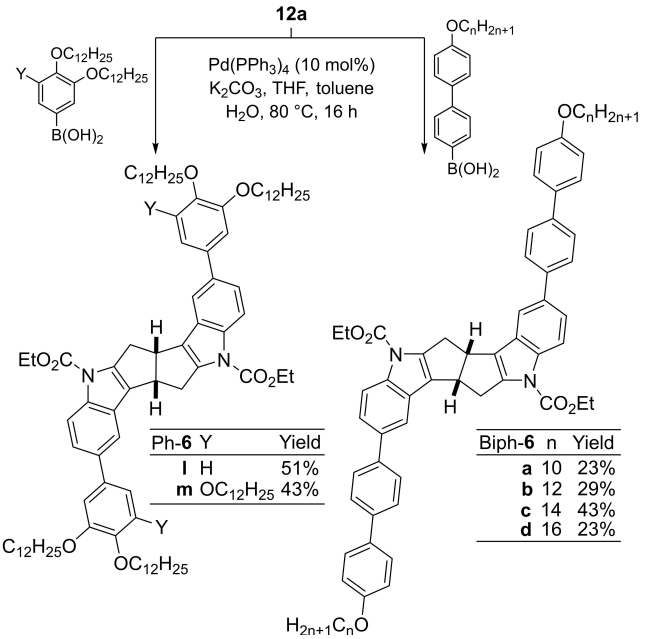
Ph-**6**	**a**	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**	**j**	**k**
R =	C_8H_{17}	$C_{10}H_{21}$	$C_{12}H_{25}$	$C_{14}H_{29}$	$C_{16}H_{33}$	$C_{12}H_{25}$	$C_{12}H_{25}$	$C_{12}H_{25}$	$C_{12}H_{25}$	$C_{12}H_{25}$	$C_{12}H_{25}$
R^1=	CO_2Et	CO_2Et	CO_2Et	CO_2Et	CO_2Et	CO_2Me	Boc	Z	Ts	Pr	$C_{12}H_{25}$
Yield (%) **A**	–	–	74	–	–	–	36	–	–	80	38
Yield (%) **B**	45	40	38	31	22	32	45	10	16	–	–

Scheme 3. Synthesis of the diindole derivatives Ph-**6** via the two routes **A** and **B**.

The target compounds **6** were accessible from dibromodiindole **9** either by running first the Suzuki coupling and subsequently the *N*-protection (route A) or the reversed order (route B). The Suzuki coupling of dibromodiindole **9** with 4-(dodecyloxy)phenylboronic acid **10c** proceeded without any event and the resulting diindole **11** was isolated in 64% (route A). Compound **11** was then used as a key intermediate to introduce the *N*-protecting groups. The reaction of **11** with ethyl chloroformate and KOH in DMF at 0 °C and warming to room temperature over 16 h gave diethyl diindoledicarboxylate Ph-**6c** in 74%. Treatment of **11** with Boc_2O in the presence of DMAP in THF following a method by Zaimoku[16] provided the Boc-protected diindole Ph-**6g** albeit with a disappointing yield of 36%. Alkylation with 1-iodopropane and 1-bromododecane, respectively, yielded the *N*-alkylated products Ph-**6j** and Ph-**6k** ($R^1 = C_3H_7$ and $C_{12}H_{25}$) in 80% and 38%.

Following route B key intermediate **9** was submitted first to the *N*-protection. The yields of the *N*-protected dibromodiindoles **12** ranged between 80% and 88%, except for the Z-protected derivative **12d**, which was isolated in only 35% (Scheme 3). The subsequent Suzuki cross-coupling of compounds **12a**–**e** with 4-(dodecyloxy)phenylboronic acid **10c** again turned out to be a certain bottleneck, providing the respective target diindoles Ph-**6c**,**f**–**i** in 10–45% yield. In order to vary the alkoxy chain lengths, *N*-protected dibromodiindole **12a** was coupled with 4-(alkoxy)phenylboronic acids **10a**–**e** to yield the diindoles Ph-**6a**–**e** in 22–45% (Scheme 3).

Furthermore, we aimed to increase the volume requirement of the side chains. For this purpose, **12a** was reacted with 3,4-bis(dodecyloxy)- and 3,4,5-tris(dodecyloxy) phenylboronic acid[17,18] to give the respective tetra- and hexa-dodecyloxy-substituted diindoles Ph-**6l** and Ph-**6m** in 51% and 43% yield (Scheme 4).



Scheme 4. Synthesis of diindole derivatives Ph-**6l**,**m** and Biph-**6**.

In addition, the aspect (lengths to breadths) ratio was increased by attaching 4′-(alkoxy)-1,1′-biphenyl units to the diindole core **12a**, and the resulting target compounds Biph-**6a**–**d** were isolated in 23–43% yield (Scheme 4).

Fortunately, single crystals of diethyl 2,8-bis(4′-decyloxy-1,1′-biphenyl)-tetrahydropentaleno[2,1-*b*:5,4-b′]diindole-5,11-dicarboxylate Biph-**6a** could be obtained, which enabled an X-ray crystal structure determination (Figure 1).[19]

Biph-**6a** crystallized with one molecule in the asymmetric unit of the centrosymmetric, triclinic space group P-1. Both terminal aliphatic chains are disordered (Figure S1). The central hydropentalene core features a folding angle between the 5-membered ring systems of 64.2(1)°, resulting in a nearly perpendicular orientation of the indole and biphenyl moieties (average about 75°). Both biphenyl units are out of plane in their orientation, but with clearly different values (24.0(3)° and 11.1(3)°, respectively). The packing diagram of the cell plot (Figure 1b) shows only a slight interdigitation of the molecules. This observation is supported by the disordered behavior of the aliphatic chains which underlines no clear orientation of them to each other. Nevertheless, we observe three types of weak intermolecular interactions, namely π-π interactions of the indole moieties characterized representatively by a N1-C13 distance of 3.40 Å, aliphatic-π interactions which have more electrostatic character, for example, between aliphatic C51 and biphenyl C38 with a distance of 3.41 Å (the distance of the donor H51A and the acceptor C38 is 2.81 Å and the relevant angle C51-H51A···C28 is 120°), and last a type of weak hydrophobic intermolecular interactions between the aliphatic chains characterized by a C57···C61 distance of 3.57 Å. The distance of the donor H57B to the acceptor C61 is 2.77 Å and the relevant angle C57-H17B···C61 is 138°.

Mesomorphic Properties of Diindoles

The liquid crystalline behavior of the synthesized diindoles **6** was first investigated by differential scanning calorimetry (DSC). Selected DSC curves are given in Figure 2. Among the differently *N*-protected diindoles only diethyl diindoledicarboxylate Ph-**6c** formed enantiotropic mesophases, whereas the other derivatives were either monotropic (Ph-**6f**,**g**) or non-mesomorphic (Ph-**6h**–**k**). The series of compounds Ph-**6a**–**e** carrying alkyloxy substituents of various chain lengths showed enantiotropic mesomorphism. The results of the DSC measurements are summarized in Table 1 and visualized in Figure 4 for comparison.

The first heating curve of Ph-**6c** showed an endothermal melting transition at 184 °C and a hardly visible weak clearing transition at 203 °C (Figure 2a). Upon first cooling, the isotropic-to-mesophase transition appeared at 206 °C, while the M→Cr_2 transition at 110 °C showed a pronounced hysteresis due to supercooling. In addition, a Cr_2→Cr_1 transition at 100 °C was detected. The phase behavior during subsequent heating/cooling cycles was fully reproducible. Under the polarizing optical microscope (POM) Schlieren textures were observed at 206 °C (Figure 3a), which are indicative of a nematic (N) phase.

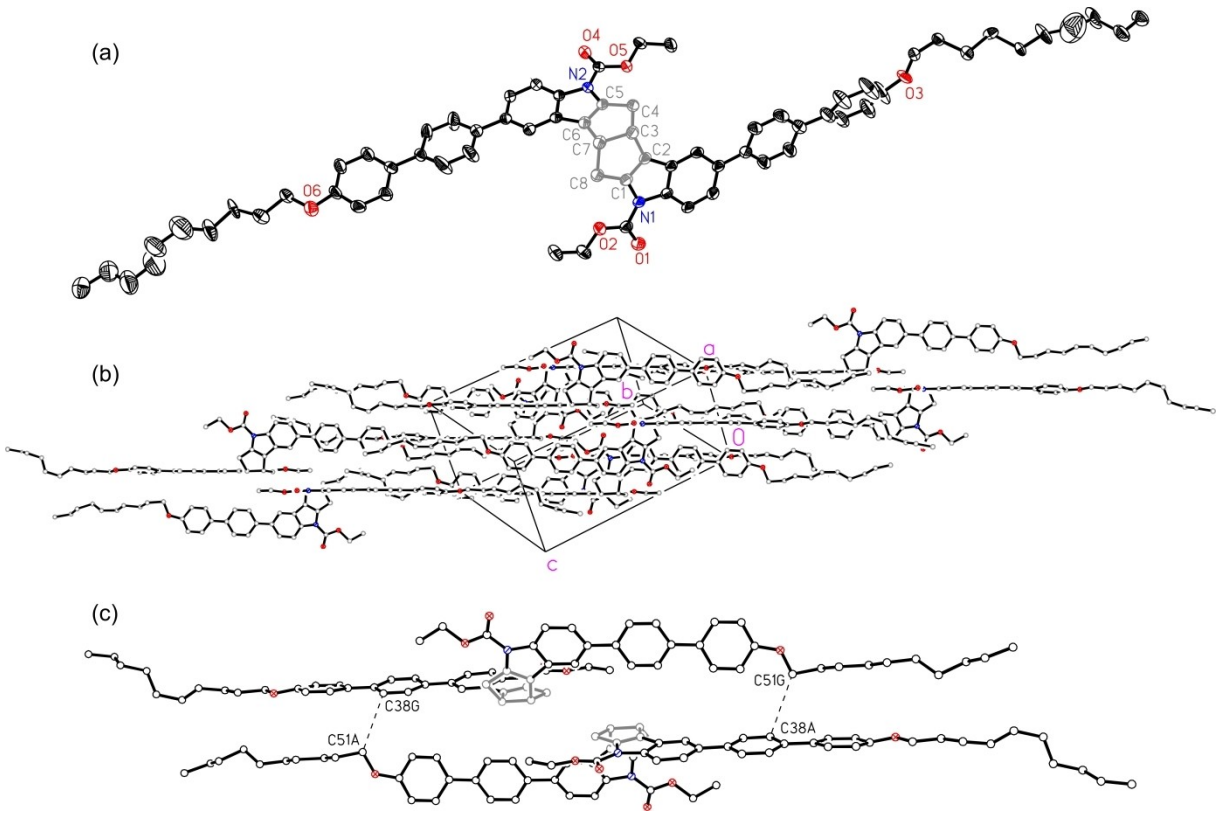


Figure 1. a) Structure of Biph-**6a** in the solid-state (central hydropentalene core in grey, H atoms omitted for clarity). b) Packing diagram of the unit cell (for clarity top view orientation to one side of the π-systems); and c) a further view on the orientation of two molecules revealing interactions between the alkyl chain and biphenyl unit.

Table 1. Phase transition temperatures [°C] and enthalpies ΔH [kJ mol^{-1}] of diindoles Ph-**6a–e** and Biph-**6a–d** upon second heating (H) and cooling (C) (rate 10 K min^{-1}).[a,b]

Compd	Phase	*T* (ΔH)	Phase	*T* (ΔH)	Phase	*T* (ΔH)	Phase	
Ph-**6a**	Cr	209 (44.5)			N	250 (1.0)	I	H
	Cr	162 (38.5)			N	249 (1.2)	I	C
Ph-**6b**	Cr	200 (62.1)			N	230 (1.1)	I	H
	Cr[c]	151 (37.6)			N	230 (1.1)	I	C
Ph-**6c**	Cr	183 (59.7)			N	203 (1.0)	I	H
	Cr[d]	110 (40.6)			N	206 (1.2)	I	C
Ph-**6d**	Cr	174 (59.0)	SmA	183 (0.2)	N	200 (0.9)	I	H
	Cr	103 (39.4)	SmA	185 (0.3)	N	200 (1.0)	I	C
Ph-**6e**	Cr	166 (56.6)	SmA	180 (0.8)	N	185 (0.8)	I	H
	Cr	97 (17.4)	SmA	181 (0.1)	N	186 (1.0)	I	C
Biph-**6a**	Cr	203 (30.2)			N	338	I (dec.)	H
Biph-**6b**	Cr	193 (16.1)	SmA	207 (60.1)	N	303	I (dec.)	H
Biph-**6c**	Cr	168 (16.3)	SmA	193 (33.9)	N	301	I (dec.)	H
Biph-**6d**	Cr	154 (19.2)	SmA	196 (29.3)	N	304	I (dec.)	H

[a] The onset of the heat flow peaks was used for the determination of the corresponding transition temperature.[20] Phases observed: Cr crystalline; N nematic; SmA smectic A; I isotropic. [b] The phase transitions of compounds Biph-**6a**-Biph-**6d** were determined upon first heating due to decomposition in subsequent cooling/heating cycles. [c] 1st heating curve was taken; an additional Cr-to-Cr transition at 132 °C. [d] Additional Cr-to-Cr transition at 104 °C.

Phenyl diindoles Ph-**6g,f** suffered from thermal decomposition already during first heating and were not further investigated (Figure S3, Figure S4, and Figure S19, Supporting Information).

A comparison of the alkoxy chain lengths reveals that the short-chain members Ph-**6a–c** with C_8, C_{10}, and C_{12} chains displayed only nematic phases, while diindoles Ph-**6d,e** with peripheral tetradecyloxy and hexadecyloxy substituents formed additional mesophases at lower temperatures (Table 1). The corresponding phase transition was hardly visible in the DSC curves but could be detected under the POM. An exemplary DSC curve is shown in Figure 2b for Ph-**6e** where an endothermal melting transition at 166 °C, an endothermal $M_1 \rightarrow M_2$ transition at 180 °C and a low-intensity clearing transition at

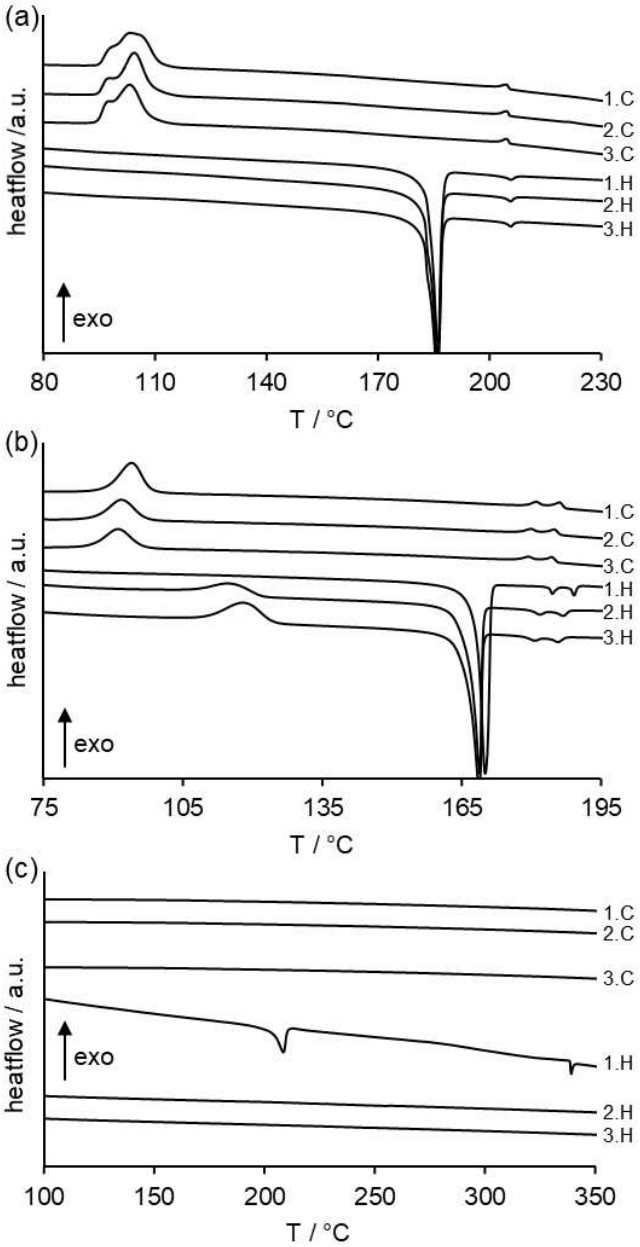


Figure 2. DSC curves of (a) phenyl diindole derivatives Ph-**6c**, (b) Ph-**6e**, and (c) 4′-(decyloxy)biphenyl diindole Biph-**6a** (c). (1.H, 2.H, 3.H relates to 1st, 2nd, and 3rd heating; 1.C, 2.C, 3.C relates to 1st, 2nd, and 3rd cooling).

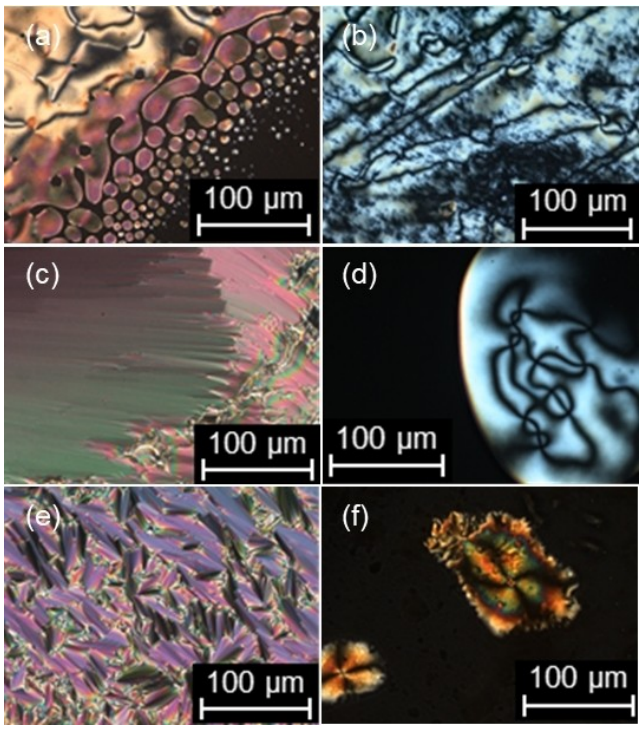


Figure 3. Textures as seen between crossed polarizers upon cooling from the isotropic liquid. (a) Nematic droplets and Schlieren texture of Ph-**6c** at 206 °C, (b) Schlieren texture of Ph-**6d** at 198 °C, (c) fan-shaped texture of Ph-**6d** at 178 °C, (d) Schlieren texture of Ph-**6e** at 183 °C, (e) fan-shaped texture of Ph-**6e** at 175 °C, and (f) Schlieren texture of Biph-**6a** at 263 °C (cooling rate 5 K min^{-1}).

185 °C upon heating were visible. Upon cooling the isotropic liquid-to-mesophase transition appeared at 186 °C, the $M_2 \rightarrow M_1$ transition at 181 °C, and the crystallization peak at 97 °C with a large hysteresis.

Under the POM a Schlieren texture was observed for Ph-**6d** at 198 °C, which persisted upon cooling until 178 °C, when a fan-shaped texture appeared, suggesting a smectic A (SmA) phase (Figure 3b, Figure 3c). Figure 3d, Figure 3e display the Schlieren and fan-shaped textures of diindole Ph-**6e** at 183 °C and 175 °C, respectively.

As shown in Figure 4a, the mesophase ranges in the series of Ph-**6a**–**e** depended on the alkoxy chain lengths. Both the melting and clearing points decreased with increasing chain lengths, resulting in nematic phase widths of 41 K (for C_8) to 5 K (for C_{16}). The phase widths of the SmA phase, however, increased slightly from 9 K (for C_{14}) to 14 K (for C_{16}). In the cooling cycle phase widths of the nematic phase for C_8-C_{12} diindoles Ph-**6a**–**c** increased significantly to 87 K, 97 K, and 96 K, respectively, due to supercooling effects. For the C_{14} and C_{16} diindoles Ph-**6d** and Ph-**6e** the same effects could be noticed for the SmA mesophases, leading to large phase widths of 82 K and 84 K, respectively.

Whereas phenyl diindoles Ph-**6l**,**m** with 4 or 6 dodecyloxy side chains were non-mesomorphic, 4′-alkoxybiphenyl-substituted diindoles Biph-**6a**–**d** were liquid crystalline. The DSC curve of Biph-**6a**, for example, revealed melting at 203 °C and a clearing point at 338 °C upon first heating (Figure 2c and Table 1). In subsequent heating/cooling scans no further transitions were detectable due to thermal decomposition, as was confirmed by thermogravimetric analysis (Figure S25). Irrespective of the chain lengths, the biphenyls Biph-**6a**–**d** were thermally stable up to 280 °C. Upon further heating, decomposition was accompanied by loss of mass. As the clearing points were located above the decomposition temperature, further characterization was done during the first heating.

Figure 4b revealed very broad nematic phase widths for Biph-**6a**–**d** ranging from 77 K (for C_{10}) to 84 K (for C_{16}). Compound Biph-**6a** only displayed a nematic phase until

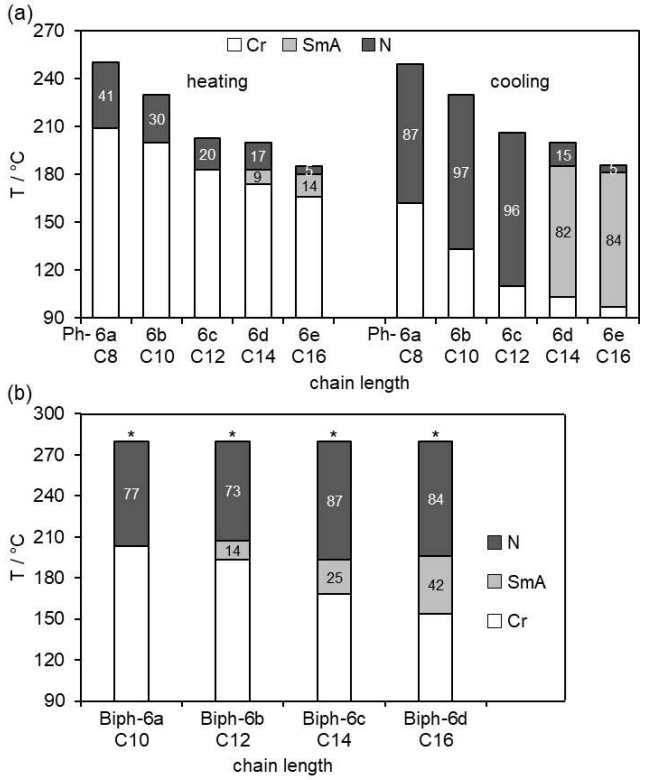


Figure 4. Mesophase widths of (a) phenyl diindoles Ph-**6a**–**e** obtained by DSC upon second heating and cooling, and (b) of Biph-**6a-d** upon first heating until the decomposition temperature (*) (heating rate 10 K min^{-1}).

decomposition, which could be due to the shorter length. Diindoles with chain lengths C_{12}-C_{16} showed additional SmA phases of 14–42 K width. With increasing chain lengths, the nematic-to-SmA transition is shifted towards lower temperature and so the more structured low-temperature SmA phase is observed to a higher degree. The extension of the aspect ratio has increased the stability of the nematic phase but at the expense of thermal decomposition of the compounds.

Under the POM a Schlieren texture was observed for Biph-**6a** at 263 °C (Figure 3f). The higher homolog Biph-**6b** displayed fan-shaped textures, whereas diindoles Biph-**6c**,**d** with C_{14} and C_{16} side chains showed focal-conic defects, indicating a SmA phase (Figures S13–S15).

X-Ray diffraction (XRD) experiments gave more insight into the phase geometries of the liquid crystalline diindoles. The XRD data are summarized in Table 2. The wide-angle X-ray scattering profile and the diffraction pattern of an oriented nematic phase of Ph-**6a** at 230 °C are given in Figure 5a.

The reflection in the small-angle region is broadened due to the lack of a positional long-range order in the N phase. In the corresponding diffraction pattern, two diffuse peaks in the small-angle and two perpendicularly oriented (induced by magnetic preorientation of the sample) arch-shaped broad reflexes in the wide-angle regime are visible, which are characteristic of a nematic phase.[21] In contrast, the WAXS profile of diindole Ph-**6d** in the SmA phase at 161 °C revealed a sharp (001) reflection in the small-angle range and a diffuse signal (halo) in the wide-angle section (Figure 5b and Table 2).

Table 2. XRD data of diindoles Ph-**6d**,**e** and Biph-**6b**–**d**.

Compound	Phase	T [°C]	d [Å]	Miller Indices
Ph-**6d**	SmA	161	40.78	(001)
			4.47	Halo
Ph-**6e**	SmA	159	42.21	(001)
			4.55	Halo
Biph-**6b**	SmA	220	46.13	(001)
			4.25	Halo
Biph-**6c**	SmA	220	49.69	(001)
			4.50	Halo
Biph-**6d**	SmA	244	53.02	(001)
			4.43	Halo

As seen in Figure 6a for diindole Ph-**6d**, temperature-dependent SAXS measurements of the (001) reflection showed a decrease of the layer distance d with increasing temperature, which is typical for SmA phases.[22] Similar results were obtained for the C_{16} diindole Ph-**6e** (Figures S32–S34). The experimentally determined layer distance d_{001} = 39.46 Å at 200 °C for Ph-**6d** is somewhat smaller than the calculated fully stretched all-*trans* molecular length of 53.3 Å.[23] Usually, interdigitation of alkyl chains is observed in lamellar phases with bilayers and is rather uncommon in monolayers due to lack of space. However, due to their nature, the cores of the diindoles take up a lot of space, which creates free volume that can be filled by interdigitation of the alkyl chains. Assuming fully interdigitated alkyl chains (Figure 6b), a smectic layer would thus consist of the length of the core (for Ph-**6d**: 19.0 Å) and the length of the alkyl chain (for Ph-**6d**: 18.6 Å), resulting in a total length of d_{calc} = 37.6 Å, which is close to the experimentally determined value of d_{001} = 39.46 Å for Ph-**6d**. This deviation from the d_{001}-value can be explained by differences in temperature or discrepancies in calculated molecule shape to the real shape of the diindoles. Experimental layer distances for the C_{16} compound Ph-**6e** (d = 42.21 Å at 159 °C) show similar behavior in comparison with Ph-**6d**.

XRD studies of the biphenyl diindole series Biph-**6a**–**d** agreed well with the results of the liquid crystalline phenyl diindoles Ph-**6**. For example, the WAXS diffractogram of derivative Biph-**6c** in the low-temperature mesophase at 200 °C revealed a distinct (001) layer reflex at small angles and in the wide-angle section a broad halo at 4.50 Å (Figure 5c). Temperature-dependent XRD measurements of the (001) reflections further supported the SmA assignment and provided layer distances d_{001} of 46.19 Å (n = 12, 220 °C), 49.64 Å (n = 14, 218 °C) and 52.76 Å (n = 16, 220 °C) for the larger biphenyl diindoles Biph-**6b**–**d** with different chain lengths, which is in good agreement to the SmA packing model provided in Figure 6b. The WAXS diffraction pattern of Biph-**6c** in the high-temperature mesophase resembled that of the N phase of Ph-**6a** (Figure 5a), displaying two diffuse reflections in the small-angle region and the arch-like halo perpendicular to the reflections.

While the X-ray crystal structure of biphenyl diindole Biph-**6a** revealed a partial overlap of the alkyl side chains and aromatic units in the crystalline solid, a nematic phase showing

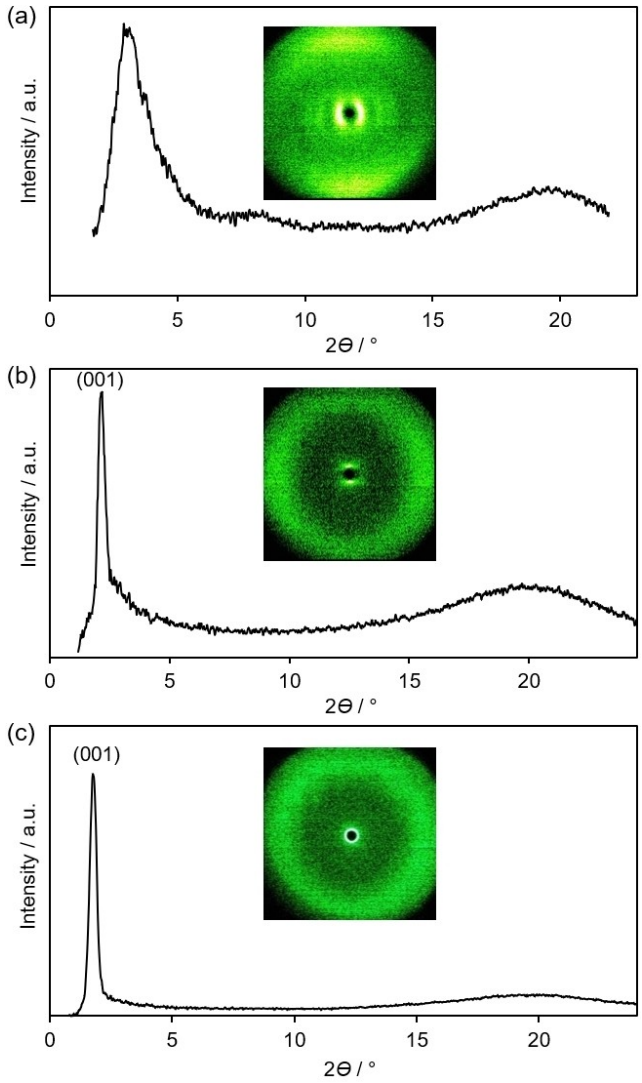


Figure 5. Wide-angle X-ray scattering (WAXS) profiles of (a) Ph-**6a** in the nematic (N) phase at 230 °C, (b) Ph-**6d** in the SmA phase at 161 °C, and (c) Biph-**6c** in the SmA phase at 200 °C. Inset: the corresponding diffraction pattern.

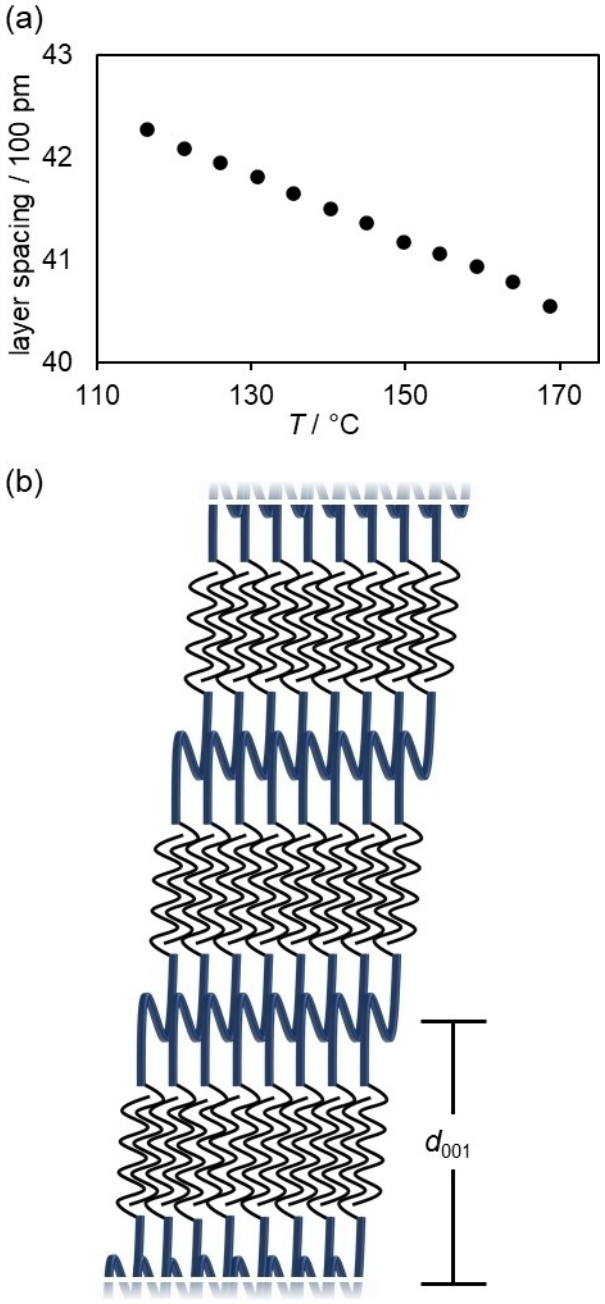


Figure 6. (a) Temperature-dependent SAXS layer distances d_{001} for phenyl diindole Ph-**6d** and (b) schematic illustration of the proposed packing of Ph-**6d** in the SmA phase.

only 1D long-range orientational order was detected by XRD for this particular derivative. Upon increasing the chain lengths in the biphenyl series, van der Waals interactions between the side chains increased, resulting in increased nanosegregation and formation of lamellar SmA phases in addition to the N phases, as was shown by XRD studies for Biph-**6b**-Biph-**6d**. In contrast, increasing the number of side chains in the phenyl series resulted in a significant decrease of the melting point for Ph-**6m** with six peripheral side chains while simultaneously suppressing mesophase formation. This is probably due to the large difference in volume requirements of the core unit and the side chains, which do not allow self-assembly into a stable mesophase.

Conclusion

A new family of indole-containing rigid, concave-shaped calamitic liquid crystals was prepared by a twofold Fischer indole synthesis as the key step. From a practical point of view, it was found advantageous to convert the dibromodiindole intermediate **9** into the target diindoles Ph-**6** and Biph-**6** via sequential *N*-protection / Suzuki cross-coupling rather than using the reversed sequence.

The *N*-protecting group had a major impact on the liquid crystalline self-assembly. Among all tested protecting groups (Boc, CO_2Me, CO_2Et, Z, Me, *n*-propyl, *n*-dodecyl, Ts) only the ethylcarbamate led to stable mesophases and reproducible phase behavior.

Chain length variation in the series of phenyl diindoles Ph-**6a**–**e** (C_8-C_{16}) resulted in destabilization of the nematic phase with increasing chain lengths, whereas SmA phases were stabilized. An increase of the total number of alkoxy substituents from 2 to 4 or 6 led to the loss of mesophases.

On the other hand, an increase of the aspect ratio by extending the hexacyclic diindole core with peripheral alkyloxybiphenyl instead of alkyloxyphenyl significantly stabilized the nematic phase. However, in agreement with the old saying "every magic comes with a price" the increase of the aspect ratio of Biph-**6** led to clearing points above the decomposition temperature of 280 °C. From the XRD results a packing model for the SmA phase was proposed, where the S-shaped rigid cores arrange themselves in an interdigitated monolayer, which is in agreement with the solid-state packing of Biph-**6a**.

Our results reveal that the steric isolation of the two indole moieties by a saturated hydropentalene core together with the choice of suitable carbamate protecting group indeed lead to stable calamitic indoles suitable for further exploration as organic soft matter materials.

Experimental Section

General. All chemicals were used as purchased. Anhydrous solvents were dried and distilled under nitrogen atmosphere prior to use. All reactions were carried out under a nitrogen atmosphere with Schlenk-type glassware unless otherwise stated. NMR spectra were recorded on Bruker Avance 400, 500 or 700 MHz instruments. All chemical shifts (δ) are given in ppm and are referenced to tetramethylsilane as an internal standard unless otherwise stated. Assignment of the resonances was supported by 2D experiments (COSY and HMBC). IR spectra were recorded on a Bruker Vektor 22 instrument equipped with a MKII Golden Gate Single Reflection Diamond ATR. MS and HRMS were measured on a Bruker micro-TOF-Q spectrometer with electrospray ionization (ESI) or on a Finnigan Varian MAT95 spectrometer with electron ionization (EI). GC-MS was performed on an Agilent Technologies 6890N Network GC system equipped with an Agilent 5973 Network Mass Selective Detector. An Olympus BX50 combined with a Linkam TP93 central controller was used for polarizing optical microscopy (POM). Differential scanning calorimetry (DSC) was carried out on a Mettler Toledo DSC822^e and X-ray diffraction (XRD) measurements on a Bruker AXS Nanostar C with ceramic tube generator (1500 W) and cross-coupled Goebel mirrors (monochromatic $Cu_{K,\alpha1}$ radiation, 1.5405 Å). Diffraction patterns were measured with a Bruker HI-STAR detector and were calibrated using a diffraction pattern of silver behenate at room temperature. The diffraction patterns were analyzed with Datasqueeze and Origin. Flash chromatography was performed on silica gel, grain size 40–63 μm (Fluka), and aluminium sheets precoated with silica gel 60 F_{254} (Merck) were used for thin-layer chromatography (TLC).

(6a*SR*,12a*SR*)-2,8-Dibromo-5,6,6a,11,12,12a-hexahydropentaleno[2,1-*b*:5,4-b′]diindole (9): To a solution of ketone **7** (1.00 g, 7.24 mmol) and 4-bromophenylhydrazine hydrochloride **8** (3.80 g, 17.0 mmol) in abs. EtOH (70 mL) Amberlite® IR 120 (10 g; hydrogen form, strongly acidic) was added, and the reaction mixture stirred at 80 °C for 16 h. After cooling to room temperature, the resin was filtered off, washed with EtOAc and the filtrate was concentrated under vacuum. The resulting solid was dissolved in EtOAc, the organic layer washed with H_2O, dried ($MgSO_4$), and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica (gradient hexanes/EtOAc 50:1→3:1) to give **9** (1.46 g, 3.31 mmol, 46%) as a yellow solid. M.p. 256–257 °C; ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 2.91–2.98 (m, 2H; 6-H$_a$, 12-H$_a$), 3.24–3.32 (m, 2H; 6-H$_b$, 12-H$_b$), 4.38–4.43 (m, 2H; 6a-H, 12a-H), 7.08 (dd, *J* = 8.8, 1.9 Hz, 2H; 3-H, 9-H), 7.22 (d, *J* = 8.8, 2H; 4-H, 10-H), 7.63 (d, *J* = 1.9 Hz, 2H; 1-H, 7-H), 10.98 ppm (s, 2H, N*H*); ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 30.8 (C-6, C-12), 46.9 (C-6a, C-12a), 111.2 (C-2, C-8), 113.6 (C-4, C-10), 119.7 (C-1, C-7), 119.8 (C-6b, C-12b), 122.0 (C-3, C-9), 125.3 (C-6c, C-12c), 139.8 (C-4a, C-10a), 144.3 ppm (C-5a, C-11a). FT-IR (ATR): $\tilde{\nu}$ = 3441 (w), 3068 (w), 2931 (w), 2844 (w), 1724 (w), 1606 (w), 1572 (w), 1466 (w), 1425 (s), 1349 (w), 1282 (s), 1221 (w), 1148 (w), 1041 (w), 976 (w), 924 (w), 863 (s), 837 (w), 796 (s), 743 (w), 693 (w), 641 (w), 582 (s) cm^{-1}; MS (ESI): *m/z* = 438.9 [*M*−H]$^-$, 324.9; HRMS (ESI): *m/z* calcd for $C_{20}H_{14}Br_2N_2$-H$^-$: 438.9440 [*M*−H]$^-$, found: 438.9435 [*M*−H]$^-$.

Diethyl (6a*SR*,12a*SR*)-2,8-dibromo-6,6a,12,12a-tetrahydropentaleno[2,1-*b*:5,4-b′]diindole-5,11-dicarboxylate (12a): To a solution of **9** (1.22 g, 2.74 mmol) in abs. DMF (25 mL) with powdered KOH (774 mg, 13.8 mmol) ethyl chloroformate (7.88 mL, 898 mg, 8.28 mmol) was slowly added at 0 °C and the reaction mixture was then stirred at room temperature for 16 h. The reaction mixture was diluted with H_2O (200 mL), and the resulting solid was filtered off, washed with EtOAc and dried to give **12a** (1.45 g, 2.26 mmol, 82%) as a colorless solid. M.p. 335 °C (dec.); due to poor solubility **12a** could not be characterized by NMR spectroscopy; FT-IR (ATR): $\tilde{\nu}$ = 3069 (w), 2982 (w), 2919 (w), 2852 (w), 1743 (s), 1728 (s), 1609 (w), 1591 (w), 1564 (w), 1476 (w), 1458 (w), 1438 (s), 1403 (s), 1376 (s), 1346 (s), 1318 (s), 1289 (w), 1274 (w), 1235 (w), 1213 (s), 1162 (w), 1125 (s), 1055 (s), 960 (w), 935 (w), 884 (w), 871 (w), 851 (w), 813 (s), 786 (w), 762 (s), 744 (w), 707 (s), 653 (w), 577 (w), 499 (w), 454 (w), 426 (w) cm^{-1}. MS (EI): *m/z* = 586.0 [*M*]$^+$ (100), 508.1 (15), 441.0 (4), 360.0 (9), 279.1 (9) 79.9 (6), 44.0 (4); HRMS (EI): *m/z* calcd for $C_{26}H_{22}Br_2N_2O_4^+$: 583.9946 [*M*]$^+$, found: 583.9942 [*M*]$^+$.

General Procedure for the Preparation of Carbamate-protected Diindoles (GP1): To a solution of **9** (430 μmol) in abs. CH_2Cl_2 (20 mL) with powdered NaOH (2.15 mmol) and Bu_4NBr (43.0 μmol) the appropriate formate (1.29 mmol) was added and the reaction mixture stirred at room temperature for 16 h. The formed suspension was mixed with H_2O (3×20 mL) and the resulting solid was filtered off, washed with Et_2O (2×20 mL) and dried.

Dimethyl (6a*SR*,12a*SR*)-2,8-dibromo-6,6a,12,12a-tetrahydropentaleno[2,1-*b*:5,4-b′]diindole-5,11-dicarboxylate (12b): According to GP1, from **9** (190 mg, 430 μmol), NaOH (86.0 mg, 2.15 mmol), Bu_4NBr (14.0 mg, 43.0 μmol), methyl formate (0.80 mL, 77.0 mg, 1.29 mmol); yield: 210 mg, 376 μmol, 88%, colorless solid; m.p. > 350 °C; due to poor solubility **12b** could not be characterized by NMR spectroscopy; FT-IR (ATR): $\tilde{\nu}$ = 3333 (w), 3108 (w), 2916 (s), 2848 (s), 1732 (s), 1613 (w), 1593 (w), 1562 (w), 1462 (s), 1439 (s), 1398 (w), 1368 (s), 1336 (w), 1319 (s), 1284 (w), 1258 (w), 1235 (w), 1213 (s), 1164 (w), 1127 (s), 1089 (w), 1049 (s), 999 (w), 952 (w), 937 (w), 879 (w), 862 (w), 812 (s), 784 (w), 759 (s), 745 (w), 729 (w), 708 (s), 660 (w), 579 (w), 542 (w), 499 (w), 433 (w) cm^{-1}; MS (ESI): *m/z* = 580.95 [*M*+Na]$^+$, 393.30, 301.14; HRMS (ESI): *m/z* calcd for $C_{24}H_{18}Br_2N_2O_4^+$: 578.9526 [*M*+Na]$^+$, found: 578.9520 [*M*+Na]$^+$.

Di-*tert*-butyl (6a*SR*,12a*SR*)-2,8-dibromo-6,6a,12,12a-tetrahydropentaleno[2,1-*b*:5,4-b′]diindole-5,11-dicarboxylate (12c): To a solution of **9** (125 mg, 283 μmol) in abs. THF (50 mL) di-*tert*-butyl dicarbonate (148 mg, 676 μmol) and 4-dimethylaminopyridine

(3.00 mg, 28.3 μmol) were added and the reaction mixture was stirred at room temperature for 5 h. The reaction mixture was then washed with a satd solution of $NaHCO_3$ (15 mL) and extracted with EtOAc (3×20 mL). The combined organic layers were washed with H_2O (3×20 mL), dried ($MgSO_4$), and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica with hexanes/EtOAc (5:1) to give **12c** (147 mg, 228 μmol, 81%) as a colorless solid; m.p. 236 °C; ^{1}H NMR (700 MHz, $CDCl_3$): δ = 1.62 (s, 18H; CH_3), 3.21–3.31 (m, 2H; 6-H_a, 12-H_a), 3.44–3.54 (m, 2H; 6-H_b, 12-H_b), 4.30–4.52 (m, 2H; 6a-H, 12a-H), 7.32 (dd, *J* = 8.8, 1.9 Hz, 2H; 3-H, 9-H), 7.59 (d, *J* = 1.9 Hz, 2H; 1-H, 7-H), 7.98 ppm (d, *J* = 8.8 Hz, 2H; 4-H, 10-H); ^{13}C NMR (176 MHz, $CDCl_3$): δ = 28.2 (CH_3), 33.9 (C-6, C-12), 45.7 (C-6a, C-12a), 84.0 (C(CH$_3$)$_3$), 116.1 (C-2, C-8), 117.4 (C-4, C-10), 120.8 (C-1, C-7), 125.3 (C-6b, C-12b), 125.8 (C-3, C-9), 127.5 (C-6c, C-12c), 139.0 (C-4a, C-10a), 143.3 (C-5a, C-11a), 149.4 ppm (NCOO); FT-IR (ATR): $\tilde{\nu}$ = 3005 (w), 2975 (w), 2927 (w), 2856 (w), 1728 (s), 1612 (w), 1593 (w), 1561 (w), 1474 (w), 1458 (w), 1433 (w), 1402 (w), 1391 (w), 1365 (s), 1335 (w), 1319 (w), 1272 (w), 1256 (w), 1233 (w), 1216 (w), 1158 (w), 1123 (s), 1054 (w), 1027 (w), 933 (w), 908 (w), 881 (w), 856 (w), 837 (w), 814 (w), 806 (w), 767 (w), 733 (w), 703 (w), 674 (w), 650 (w), 578 (w), 498 (w), 462 (w), 426 (w) cm^{-1}; MS (ESI): *m/z* = 663.45 [*M* + Na]$^+$, 597.4, 447.34, 391.28, 371.31, 333.16, 305.13; HRMS (ESI): *m/z* calcd for $C_{30}H_{30}Br_2N_2O_4$ + Na^+: 663.0465 [*M* + Na]$^+$, found: 663.0468 [*M* + Na]$^+$.

Dibenzyl (6a*SR*,12a*SR*)-2,8-dibromo-6,6a,12,12a-tetrahydropentaleno[2,1-*b*:5,4-b′]diindole-5,11-dicarboxylate (12d): According to GP1, from **9** (130 mg, 294 μmol), NaOH (30.0 mg, 747 μmol), Bu_4NBr (7.00 mg, 20.6 μmol), benzyl chloroformate (1.00 mL, 120 mg, 705 μmol), yield: 66.0 mg, 92.9 μmol, 32%, colorless solid; m.p. 305 °C; due to poor solubility **12d** could not be characterized by NMR spectroscopy; FT-IR (ATR): $\tilde{\nu}$ = 3066 (w), 3031 (w), 2936 (w), 2862 (w), 1732 (s), 1614 (w), 1598 (w), 1566 (w), 1500 (w), 1456 (w), 1443 (w), 1400 (s), 1352 (s), 1334 (w), 1314 (s), 1271 (w), 1257 (w), 1209 (s), 1157 (w), 1125 (s), 1057 (s), 1035 (w), 985 (w), 942 (w), 899 (w), 858 (w), 836 (w), 809 (s), 763 (w), 742 (s), 712 (w), 691 (s), 651 (w), 584 (w), 506 (w), 496 (w), 425 (w) cm^{-1}; MS (ESI): *m/z* = 733.01 [*M* + Na]$^+$, 503.35, 459.32, 415.30, 381.29, 353.26; HRMS (ESI): *m/z* calcd for $C_{36}H_{26}Br_2N_2O_4$ + Na^+: 731.02 [*M* + Na]$^+$, found: 731.01 [*M* + Na]$^+$.

(6a*SR*,12a*SR*)-2,8-Dibromo-5,11-ditosyl-5,6,6a,11,12,12a-hexahydropentaleno[2,1-*b*:5,4-b′]diindole (12e): To a solution of **9** (180 mg, 407 μmol) in abs. CH_2Cl_2 (20 mL) with powdered NaOH (81.0 mg, 2.04 mmol) and Bu_4NBr (14.0 mg, 40.7 μmol) *p*-toluenesulfonic acid chloride (163 mg, 855 μmol) was added and the reaction mixture was stirred at room temperature for 16 h. The reaction mixture was washed with H_2O (15 mL), dried ($MgSO_4$), and the solvent was removed under vacuum. The crude product was dissolved in CH_2Cl_2 (5 mL), precipitated with Et_2O and filtered off to give **12e** (243 mg, 324 μmol, 80%) as a colorless solid. M.p. 277 °C; ^{1}H NMR (400 MHz, [D$_8$]THF): δ = 2.20 (s, 6H; 5′-H), 3.28–3.38 (m, 2H; 6-H_a, 12-H_a), 3.45-3.56 (m, 2H; 6-H_b, 12-H_b), 4.31–4.41 (m, 2H; 6a-H, 12a-H), 6.99 (d, *J* = 8.4 Hz, 4H; 3′-H), 7.37 (dd, *J* = 8.8, 2.0 Hz, 2H; 3-H, 9-H), 7.54 (d, *J* = 8.4 Hz, 4H; 2′-H), 7.73 (d, *J* = 2.0 Hz, 2H; 1-H, 7-H), 7.92 ppm (d, *J* = 8.8 Hz, 2H; 4-H, 10-H); ^{13}C NMR (101 MHz, [D$_8$]THF): δ = 21.4 (C-5′), 33.4 (C-6, C-12), 47.2 (C-6a, C-12a), 116.9 (C-4, C-10), 117.7 (C-2, C-8), 122.4 (C-1, C-7), 126.9 (C-3, C-9), 127.3 (C-2′), 127.7 (C-6b, C-12b), 129.1 (C-6c, C-12c), 130.6 (C-3′), 136.3 (C-1′), 140.1 (C-4a, C-10a), 144.6 (C-5a, C-11a), 146.0 ppm (C-4′); FT-IR (ATR): $\tilde{\nu}$ = 2921 (w), 2852 (w), 1721 (w), 1596 (w), 1560 (w), 1494 (w), 1454 (w), 1431 (w), 1389 (w), 1367 (w), 1329 (w), 1305 (w), 1268 (w), 1251 (w), 1218 (w), 1187 (w), 1170 (s), 1127 (w), 1089 (w), 1056 (w), 1023 (w), 1004 (w), 939 (w), 906 (w), 862 (w), 829 (w), 807 (s), 738 (w), 702 (w), 682 (w), 664 (s), 581 (s), 564 (w), 539 (s), 494 (w), 422 (w) cm^{-1}; MS (APCI): *m/z* = 750.98 [*M* + H]$^+$, 595.96 [*M* − 2Ts]$^+$, 363.97; HRMS (APCI): *m/z* calcd for $C_{34}H_{26}Br_2N_2O_4S_2$ + H^+: 748.9773 [*M* + H]$^+$, found: 748.978 [*M* + H]$^+$.

General Procedure for the Preparation of Alkoxy-protected Diindoles (GP2): To a solution of the respective diindole (351 μmol) in abs. DMF (5 mL) with powdered KOH (49.0 mg, 876 μmol) the appropriate 1-bromoalkane (876 μmol) was added and the reaction mixture was stirred at room temperature for 16 h. The reaction mixture was washed with H_2O (15 mL), and extracted with CH_2Cl_2 (3×20 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was removed under vacuum. The crude products were either recrystallized from Et_2O/EtOAc or purified by column chromatography on silica gel.

(6a*SR*,12a*SR*)-5,11-Dipropyl-2,8-bis(4-dodecyloxyphenyl)-5,6,6a,11,12,12a-hexahydropentaleno[2,1-*b*:5,4-*b*′]diindole (Ph-6j): According to GP2, from **11** (100 mg, 124 μmol), KOH (35.0 mg, 621 μmol), 1-bromopropane (0.60 mL, 106 mg, 621 μmol), column chromatography with CH_2Cl_2/hexanes (1:5); yield: 88.0 mg, 98.9 μmol, 80%, colorless solid, m.p. 167 °C; ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.3 Hz, 12H; CH_3), 1.24–1.41 (m, 32H; CH_2), 1.45–1.52 (m, 4H; CH_2), 1.71–1.85 (m, 8H; CH_2), 3.10–3.18 (m, 2H; 6-H_a, 12-H_a), 3.29–3.39 (m, 2H; 6-H_b, 12-H_b), 3.81–3.97 (m, 4H; NCH_2), 4.01 (t, *J* = 6.7 Hz, 4H; OCH_2), 4.58–4.66 (m, 2H; 6a-H, 12a-H), 6.98 (d, *J* = 8.6 Hz, 4H; 3′-H), 7.24–7.27 (m, 2H; 3-H, 9-H), 7.30 (d, *J* = 8.5 Hz, 2H; 1-H, 7-H), 7.59 (d, *J* = 8.7 Hz, 4H; 2′-H), 7.67–7.72 ppm (m, 2H; 4-H, 10-H); ^{13}C NMR (176 MHz, $CDCl_3$): δ = 11.6 (NCH$_2$CH$_2$CH_3), 14.1 (CH_3), 22.7, 23.6, 26.1, 29.4, 29.4, 29.6, 29.7, 30.2, 31.0 (CH_2), 31.9 (C-6, C-12), 46.5 (NCH_2), 47.4 (C-6a, C-12a), 68.1 (OCH_2), 109.9 (C-3, C-9), 114.7 (C-3′), 116.2 (C-4, C-10), 119.3 (C-6b, C-12b), 120.0 (C-1, C-7), 124.3 (C-6c, C-12c), 128.2 (C-2′), 132.1 (C-2, C-8), 135.3 (C-1′), 140.4 (C-4a, C-10a), 145.2 (C-5a, C-11a), 157.9 ppm (C-4′); FT-IR (ATR): $\tilde{\nu}$ = 3037 (w), 2954 (w), 2919 (s), 2851 (s), 1609 (w), 1575 (w), 1516 (s), 1467 (s), 1432 (w), 1358 (w), 1324 (w), 1302 (w), 1272 (s), 1245 (s), 1176 (w), 1127 (w), 1109 (w), 1030 (w), 946 (w), 875 (w), 831 (w), 801 (s), 720 (w), 630 (w), 610 (w), 529 (w), 437 (w) cm^{-1}; MS (APCI): *m/z* = 889.66 [*M* + H]$^+$, 456.33, 432.32; HRMS (ESI): *m/z* calcd for $C_{62}H_{84}N_2O_2$ + H^+: 889.6606 [*M* + H]$^+$, found: 889.6609 [*M* + H]$^+$.

(6a*SR*,12a*SR*)-5,11-Didodecyl-2,8-bis(4-dodecyloxyphenyl)-5,6,6a,11,12,12a-hexahydropentaleno[2,1-*b*:5,4-*b*′]diindole (Ph-6k): According to GP2, from **11** (50.0 mg, 62.1 μmol), KOH (9.00 mg, 155 μmol), 1-bromododecane (0.39 mL, 39.0 mg, 155 μmol), recrystallization from EtOAc; yield: 27.0 mg, 23.6 μmol, 38%, colorless solid, m.p. 129 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.80–0.92 (m, 12H; CH_3), 1.14–1.42 (m, 68H; CH_2), 1.42–1.61 (m, 4H; CH_2), 1.61–1.76 (m, 4H; CH_2), 1.76–1.87 (m, 4H; CH_2), 3.07–3.19 (m, 2H; 6-H_a, 12-H_a), 3.26–3.39 (m, 2H; 6-H_b, 12-H_b), 3.81–3.96 (m, 4H; NCH_2), 4.01 (t, *J* = 6.6 Hz, 4H; OCH_2), 4.55–4.68 (m, 2H; 6a-H, 12a-H), 6.98 (d, *J* = 8.4 Hz, 4H; 3′-H), 7.25–7.27 (m, 2H; 4-H, 10-H), 7.30 (dd, *J* = 8.5, 1.6 Hz, 2H; 3-H, 9-H), 7.58 (d, *J* = 8.4 Hz, 4H; 2′-H), 7.69 ppm (d, *J* = 1.6 Hz, 2H; 1-H, 7-H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7 (CH_3), 22.7, 26.1, 27.1, 29.3, 29.3, 29.4, 29.4, 29.5, 29.5, 29.6, 29.6, 29.6, 29.6, 29.7, 29.7, 30.3, 31.0 (CH_2), 31.9 (C-6, C-12), 31.9 (CH_2), 44.9 (NCH_2), 47.5 (C-6a, C-12a), 68.1 (OCH_2), 109.9 (C-4, C-10), 114.7 (C-3′), 116.2 (C-1, C-7), 119.3 (C-6b, C-12b), 120.0 (C-3, C-9), 124.3 (C-6c, C-12c), 128.2 (C-2′), 132.1 (C-2, C-8), 135.4 (C-1′), 140.3 (C-4a, C-10a), 145.2 (C-5a, C-11a), 157.9 ppm (C-4′); FT-IR (ATR): $\tilde{\nu}$ = 2955 (w), 2918 (s), 2850 (s), 1715 (w), 1608 (w), 1576 (w), 1514 (w), 1461 (s), 1366 (w), 1242 (s), 1181 (w), 1140 (w), 1113 (w), 1029 (w), 870 (w), 829 (w), 801 (w), 772 (w), 721 (w), 640 (w), 610 (w), 575 (w), 531 (w), 435 (w) cm^{-1}; MS (APCI): *m/z* = 1141.93 [*M* + H]$^+$, 1073.63, 973.75, 922.01, 663.45, 622.03, 551.50, 443.23; HRMS (APCI): *m/z* calcd for $C_{80}H_{120}N_2O_2$ + H^+: 1141.9423 [*M* + H]$^+$, found: 1141.9374 [*M* + H]$^+$.

General Procedure for the Suzuki-Coupling (GP3): The appropriate diindole **9**, **12a–e** (226 μmol) was dried under vacuum with the respective boronic acid **10a–e** (905 μmol), K_2CO_3 (2.26 mmol) and

$Pd(PPh_3)_4$ (45.2 μmol) prior to dissolving in abs. THF/abs. toluene (22 mL, 1:1, v/v) and degassed H_2O (10 mL) under nitrogen atmosphere. The reaction mixture was stirred at 80 °C for 16 h. After cooling to room temperature, the reaction mixture was diluted with H_2O and EtOAc and purified by method A or B. Method A: the organic layer was dried ($MgSO_4$) and the solvent was evaporated. The resulting solid was purified by column chromatography on silica as indicated for each compound. Method B: the precipitated solid was filtered off, washed with EtOAc, and dried.

2,8-Bis(4-(dodecyloxy)phenyl)-5,6,6a,11,12,12a-hexahydropentaleno[2,1-*b*:5,4-*b*′]diindole (11): According to GP3, from **9** (100 mg, 226 μmol), **10c** (277 mg, 905 μmol), K_2CO_3 (313 mg, 2.26 mmol), $Pd(PPh_3)_4$ (52.0 mg, 45.2 μmol); purification method A: chromatography with hexanes/EtOAc (25:1); yield: 117 mg, 145 μmol, 64%, colorless solid; ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 0.88 (t, *J* = 7.1 Hz, 6H; C*H*$_3$), 1.22–1.40 (m, 32H; C*H*$_2$), 1.44–1.52 (m, 4H; C*H*$_2$), 1.77–1.85 (m, 4H; C*H*$_2$), 3.07–3.14 (m, 2H; 6-H$_a$, 12-H$_a$), 3.25–3.34 (m, 2H; 6-H$_b$, 12-H$_b$), 3.99 (t, *J* = 6.5 Hz, 4H; OC*H*$_2$), 4.52–4.58 (m, 2H; 6a-H, 12a-H), 6.98 (d, *J* = 8.6 Hz, 4H; 3′-H), 7.21–7.29 (m, 4H; 1-H, 3-H, 7-H, 9-H), 7.56 (d, *J* = 8.6 Hz, 4H; 2′-H), 7.62 (br s, 2H; NH), 7.66–7.69 ppm (m, 2H; 4-H, 10-H); ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 14.1 (*C*H$_3$), 22.7, 26.1, 29.4, 29.4, 29.6, 29.6, 29.7, 29.7 (*C*H$_2$), 31.3 (C-6, C-12), 31.9 (*C*H$_2$), 47.6 (C-6a, C-12a), 68.1 (O*C*H$_2$), 111.6 (C-1, C-7), 114.7 (C-3′), 116.1 (C-4, C-10), 120.1 (C-3, C-9), 122.0 (C-2, C-8), 124.6 (C-6b, C-12b), 128.2 (C-2′), 132.8 (C-6c, C-12c), 135.2 (C-1′), 140.4 (C-4a, C-10a), 142.7 (C-5a, C-11a), 158.0 ppm (C-4′); FT-IR (ATR): $\tilde{\nu}$ = 3397 (w), 3033 (w), 2920 (s), 2851 (s), 1738 (w), 1607 (w), 1577 (w), 1513 (s), 1456 (s), 1390 (w), 1353 (w), 1269 (w), 1237 (s), 1077 (w), 1135 (w), 1101 (w), 1031 (w), 985 (w), 928 (w), 875 (w), 833 (s), 801 (s), 722 (m), 680 (w), 616 (w), 597 (w), 534 (w) cm^{-1}; MS (ESI): *m/z* = 804.6 [*M*]$^+$, 554.4, 278.2, 110.0; HRMS (ESI): *m/z* calcd for $C_{56}H_{72}N_2O_2^+$: 804.5594 [*M*]$^+$, found: 804.5601 [*M*]$^+$. DSC: Cr 212 °C (7.5 kJ mol^{-1}) SmA 242 °C (5.4 kJ mol^{-1}) I (2.heating).

Diethyl (6a*SR*,12a*SR*)-2,8-bis(4-(octyloxy)phenyl)-6,6a,12,12a-tetrahydropentaleno[2,1-*b*:5,4-*b*′]diindole-5,11-dicarboxylate (Ph-**6a**): According to GP3, from **12a** (305 mg, 520 μmol), **10a** (390 mg, 1.56 mmol), K_2CO_3 (216 mg, 1.56 mmol), $Pd(PPh_3)_4$ (60.0 mg, 52.0 μmol), purification method B; yield: 198 mg, 237 μmol, 45%, colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 6.8 Hz, 6H; C*H*$_3$), 1.23–1.39 (m, 16H; C*H*$_2$), 1.41 (t, *J* = 7.1 Hz, 6H; COOCH$_2$C*H*$_3$), 1.45–1.53 (m, 4H; C*H*$_2$), 1.77–1.86 (m, 4H; C*H*$_2$), 3.35–3.41 (m, 2H; 6-H$_a$, 12-H$_a$), 3.50–3.58 (m, 2H; 6-H$_b$, 12-H$_b$), 4.01 (t, *J* = 6.6 Hz, 4H; OC*H*$_2$), 4.34-4.48 (m, 6H; COOC*H*$_2$, 6a-H, 12a-H), 6.99 (d, *J* = 8.8 Hz, 4H; 3′-H), 7.43 (dd, *J* = 8.6, 1.9 Hz, 2H; 3-H, 9-H), 7.58 (d, *J* = 8.8 Hz, 4H; 2′-H), 7.64 (d, *J* = 1.9 Hz, 2H; 1-H, 7-H), 8.14 ppm (d, *J* = 8.6 Hz, 2H; 4-H, 10-H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 14.5 (CO$_2$CH$_2$*C*H$_3$), 22.7, 26.1, 29.3, 29.3, 29.4, 31.8 (*C*H$_2$), 33.8 (C-6,C-12), 46.0 (C-6a, C-12a), 62.9 (COO*C*H$_2$), 68.1 (O*C*H$_2$), 114.8 (C-3′), 116.1 (C-4, C-10), 116.3 (C-1, C-7), 122.4 (C-3, C-9), 126.6 (C-6b, C-12b), 126.8 (C-6c, C-12c), 128.3 (C-2′), 134.1 (C-1′), 136.0 (C-2, C-8), 139.4 (C-4a, C-10a), 142.3 (C-5a, C-11a), 151.1 (NCOO), 158.5 (C-4′); FT-IR (ATR): $\tilde{\nu}$ = 3036 (w), 2923 (w), 2854 (w), 1729 (s), 1607 (w), 1580 (w), 1517 (w), 1459 (s), 1400 (w), 1377 (s), 1352 (w), 1332 (s), 1303 (w), 1293 (w), 1262 (s), 1251 (s), 1215 (s), 1184 (w), 1141 (w), 1118 (s), 1046 (w), 1030 (w), 971 (w), 909 (w), 873 (w), 836 (w), 814 (s), 763 (w), 725 (w), 691 (w), 608 (w), 572 (w), 531 (w), 434 (w) cm^{-1}; MS (EI): *m/z* (%) = 836.4 (100) [*M*]$^+$, 808.4 (3), 764.4 (8), 466.2 (3), 418.2 (3), 306.1 (3); HRMS (EI): *m/z* calcd for $C_{54}H_{64}N_2O_6$: 836.4764 [*M*]$^+$, found: 836.4743 [*M*]$^+$; elemental analysis calcd (%) for $C_{54}H_{64}N_2O_6$: C 77.48, H 7.71, N 3.35; found: C 77.26, H 7.52, N 3.24.

Diethyl (6a*SR*,12a*SR*)-2,8-bis(4-(decyloxy)phenyl)-6,6a,12,12a-tetrahydropentaleno[2,1-*b*:5,4-*b*′]diindole-5,11-dicarboxylate (Ph-**6b**): According to GP3, from **12a** (400 mg, 682 μmol), **10b** (569 mg, 2.05 mmol), K_2CO_3 (283 mg, 2.05 mmol), $Pd(PPh_3)_4$ (79.0 mg, 68.2 μmol), purification method B; yield: 244 mg, 273 μmol, 40%, colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.9 Hz, 6H; C*H*$_3$), 1.23–1.39 (m, 24H; C*H*$_2$), 1.42 (t, *J* = 7.1 Hz, 6H; COOCH$_2$C*H*$_3$), 1.45–1.53 (m, 4H; C*H*$_2$), 1.77–1.87 (m, 4H; C*H*$_2$), 3.34–3.44 (m, 2H; 6-H$_a$, 12-H$_a$), 3.50–3.60 (m, 2H; 6-H$_b$, 12-H$_b$), 4.01 (t, *J* = 6.6 Hz, 4H; OC*H*$_2$), 4.34–4.43 (m, 4H; COOC*H*$_2$), 4.45–4.50 (m, 2H; 6a-H, 12a-H), 7.00 (d, *J* = 8.7 Hz, 4H; 3′-H), 7.44 (dd, *J* = 8.6, 1.9 Hz, 2H; 3-H, 9-H), 7.58 (d, *J* = 8.7 Hz, 4H; 2′-H), 7.64 (d, *J* = 1.9 Hz, 2H; 1-H, 7-H), 8.15 ppm (d, *J* = 8.6 Hz, 2H; 4-H, 10-H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 14.5 (COOCH$_2$*C*H$_3$), 22.7, 26.1, 29.3, 29.4, 29.6, 29.6, 31.9 (*C*H$_2$), 33.8 (C-6, C-12), 46.0 (C-6a, C-12a), 62.9 (COO*C*H$_2$), 68.1 (O*C*H$_2$), 114.8 (C-3′), 116.1 (C-4, C-10), 116.3 (C-1, C-7), 122.4 (C-3, C-9), 126.6 (C-6b, C-12b), 126.8 (C-6c, C-12c), 128.3 (C-2′), 134.1 (C-1′), 136.0 (C-2, C-8), 139.4 (C-4a, C-10a), 142.3 (C-5a, C-11a), 151.1 (NCOO), 158.5 ppm (C-4′); FT-IR (ATR): $\tilde{\nu}$ = 3394 (w), 2913 (s), 2850 (w), 1727 (s), 1607 (w), 1580 (w), 1518 (w), 1459 (s), 1399 (w), 1376 (s), 1353 (w), 1332 (s), 1303 (w), 1293 (w), 1262 (s), 1252 (s), 1235 (w), 1215 (w), 1187 (s), 1143 (w), 1117 (s), 1047 (s), 1029 (w), 910 (w), 871 (w), 836 (w), 835 (w), 813 (s), 763 (w), 749 (w), 722 (w), 691 (w), 662 (w), 621 (w), 608 (w), 571 (w), 531 (w), 434 (w) cm^{-1}; MS (APCI): *m/z* = 949.61 [*M* + H]$^+$, 663.45, 607.39, 462.30, 394.34, 333.16; HRMS (APCI): *m/z* calcd for $C_{62}H_{80}N_2O_6 + H^+$: 949.6089 [*M* + H]$^+$, found: 949.6085 [*M* + H]$^+$; elemental analysis calcd (%) for $C_{62}H_{80}N_2O_6$: C 78.44, H 8.50, N 2.95; found: C 78.55, H 8.62, N 2.73.

Diethyl (6a*SR*,12a*SR*)-2,8-bis(4-(tetradecyloxy)phenyl)-6,6a,12,12a-tetrahydropentaleno-[2,1-*b*:5,4-*b*′]diindole-5,11-dicarboxylate (Ph-**6d**): According to GP3, from **12a** (250 mg, 426 μmol), **10d** (428 mg, 1.28 mmol), K_2CO_3 (177 mg, 1.28 mmol), $Pd(PPh_3)_4$ (49.0 mg, 42.6 μmol), purification method B; yield: 133 mg, 132 μmol, 31%, colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 6H; C*H*$_3$), 1.19–1.40 (m, 40H; C*H*$_2$), 1.42 (t, *J* = 7.1 Hz, 6H; COOCH$_2$C*H*$_3$), 1.45–1.52 (m, 4H; C*H*$_2$), 1.79–1.85 (m, 4H; C*H*$_2$), 3.33-3.45 (m, 2H; 6-H$_a$, 12-H$_a$), 3.50–3.60 (m, 2H; 6-H$_b$, 12-H$_b$), 4.02 (t, *J* = 6.5 Hz, 4H; OC*H*$_2$), 4.35–4.46 (m, 4H; COOC*H*$_2$), 4.45–4.51 (m, 2H; 6a-H, 12a-H), 7.00 (d, *J* = 8.3 Hz, 4H; 3′-H), 7.44 (dd, *J* = 8.6, 1.6 Hz, 2H; 3-H, 9-H), 7.59 (d, *J* = 8.3 Hz, 4H; 2′-H), 7.65 (d, *J* = 1.6 Hz, 2H; 1-H, 7-H), 8.15 ppm (d, *J* = 8.6 Hz, 2H; 4-H, 10-H); ^{13}C NMR (176 MHz,

$CDCl_3$): δ = 14.1 (CH_3), 14.5 ($COOCH_2CH_3$), 22.7, 26.1, 29.3, 29.4, 29.4, 29.6, 29.6, 29.7, 29.7, 29.7, 29.7, 31.9 (CH_2), 33.8 (C-6, C-12), 46.0 (C-6a, C-12a), 62.9 ($COOCH_2$), 68.1 (OCH_2), 114.8 (C-3′), 116.1 (C-4, C-10), 116.3 (C-1, C-7), 122.4 (C-3, C-9), 126.6 (C-6b, C-12b), 126.8 (C-6c, C-12c), 128.3 (C-2′), 134.1 (C-1′), 136.0 (C-2, C-8), 139.4 (C-4a, C-10a), 142.3 (C-5a, C-11a), 151.1 (NCOO), 158.5 ppm (C-4′); FT-IR (ATR): $\tilde{\nu}$ = 2918 (s), 2850 (s), 1727 (s), 1607 (w), 1580 (w), 1518 (w), 1459 (s), 1400 (s), 1377 (s), 1353 (w), 1333 (s), 1304 (w), 1293 (w), 1262 (s), 1252 (s), 1216 (s), 1187 (s), 1143 (w), 1118 (s), 1048 (w), 1025 (w), 978 (w), 909 (w), 872 (w), 836 (w), 814 (s), 764 (w), 750 (w), 733 (w), 722 (w), 692 (w), 663 (w), 609 (w), 572 (w), 532 (w), 499 (w), 435 (w) cm^{-1}; MS (ESI): *m/z* = 1027.64 $[M+Na]^+$, 685.43, 447.34, 393.29; HRMS (ESI): *m/z* calcd for $C_{66}H_{88}N_2O_6+Na^+$: 1027.6535 $[M+Na]^+$, found: 1027.6505 $[M+Na]^+$; elemental analysis calcd (%) for $C_{66}H_{88}N_2O_6$: C 78.84, H 8.82, N 2.79; found: C 78.81, H 8.64, N 2.75.

Diethyl (6a*SR*,12a*SR*)-2,8-bis(4-(hexadecyloxy)phenyl)-6,6a,12,12a-tetrahydropentaleno[2,1-*b*:5,4-*b*′]diindole-5,11-dicarboxylate (Ph-**6e**): According to GP3, from **12a** (300 mg, 512 μmol), **10e** (556 mg, 1.54 mmol), K_2CO_3 (212 mg, 1.54 mmol), $Pd(PPh_3)_4$ (59.0 mg, 51.2 μmol), purification method B; yield: 122 mg, 114 μmol, 22 %, colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 6H; CH_3), 1.20–1.38 (m, 48H; CH_2), 1.41 (t, *J* = 7.1 Hz, 6H; $COOCH_2CH_3$), 1.44–1.53 (m, 4H; CH_2), 1.74–1.87 (m, 4H; CH_2), 3.30–3.44 (m, 2H; 6-H_a, 12-H_a), 3.47–3.58 (m, 2H; 6-H_b, 12-H_b), 4.00 (t, *J* = 6.6 Hz, 4H; OCH_2), 4.33–4.44 (m, 4H; $COOCH_2$), 4.44–4.47 (m, 2H; 6a-H, 12a-H), 6.99 (d, *J* = 8.7 Hz, 4H; 3′-H), 7.43 (dd, *J* = 8.6, 1.8 Hz, 2H; 3-H, 9-H), 7.58 (d, *J* = 8.7 Hz, 4H; 2′-H), 7.64 (d, *J* = 1.8 Hz, 2H; 1-H, 7-H), 8.14 ppm (d, *J* = 8.6 Hz, 2H; 4-H, 10-H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.2 (CH_3), 14.5 ($COOCH_2CH_3$), 22.7, 26.1, 29.4, 29.4, 29.5, 29.7, 29.7, 29.7, 29.7, 29.8, 32.0 (CH_2), 33.9 (C-6, C-12), 46.0 (C-6a, C-12a), 62.9 ($COOCH_2$), 68.2 (OCH_2), 114.8 (C-3′), 116.1 (C-4, C-10), 116.3 (C-1, C-7), 122.4 (C-3, C-9), 126.6 (C-6b, C-12b), 126.9 (C-6c, C-12c), 128.3 (C-2′), 134.1 (C-1′), 136.1 (C-2, C-8), 139.4 (C-4a, C-10a), 142.4 (C-5a, C-11a), 151.1 (NCOO), 158.5 ppm (C-4′); FT-IR (ATR): $\tilde{\nu}$ = 2917 (s), 2849 (s), 1727 (s), 1607 (w), 1518 (w), 1459 (s), 1400 (s), 1377 (s), 1353 (w), 1333 (s), 1304 (w), 1293 (w), 1262 (s), 1252 (s), 1216 (s), 1188 (s), 1143 (w), 1118 (s), 1047 (w), 1026 (w), 909 (w), 872 (w), 836 (w), 814 (s), 764 (w), 733 (w), 721 (w), 692 (w), 609 (w), 572 (w), 531 (w), 505 (w), 434 (w) cm^{-1}; MS (EI): *m/z* = 1060.7 (100) $[M]^+$, 988.7 (21), 820 (4), 748.5 (4), 518.4 (5), 466.2 (4), 306.1 (11), 91.1 (5), 71.1 (5); HRMS (EI): *m/z* calcd for $C_{70}H_{96}N_2O_6^+$: 1060.7268 $[M]^+$, found: 1060.7272 $[M]^+$; elemental analysis calcd (%) for $C_{70}H_{96}N_2O_6$: C 79.20, H 9.12, N 2.64; found: C 79.08, H 8.83, N 2.45.

Dimethyl (6a*SR*,12a*SR*)-2,8-bis(4-dodecyloxyphenyl)-6,6a,12,12a-tetrahydropentaleno-[2,1-*b*:5,4-*b*′]diindole-5,11-dicarboxylate (Ph-**6f**): According to GP3, from **12b** (150 mg, 269 μmol), **10c** (329 mg, 1.07 mmol), K_2CO_3 (371 mg, 2.69 mmol), $Pd(PPh_3)_4$ (31.0 mg, 26.9 μmol), purification method A: chromatography with hexanes/EtOAc (50:1→5:1); yield: 80 mg, 86.8 μmol, 32 %, colorless solid, m.p. 184 °C; ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.0 Hz, 6H; CH_3), 1.23–1.41 (m, 32H; CH_2), 1.45–1.52 (m, 4H; CH_2), 1.82 (d, *J* = 6.7 Hz, 4H; CH_2), 3.32–3.40 (m, 2H; 6-H_a, 12-H_a), 3.47–3.57 (m, 2H; 6-H_b, 12-H_b), 3.95 (s, 6H; $COOCH_3$), 4.01 (t, *J* = 6.6 Hz, 4H; OCH_2), 4.44–4.50 (m, 2H; 6a-H, 12a-H), 7.00 (d, *J* = 8.7 Hz, 4H; 3′-H), 7.44 (dd, *J* = 8.6, 1.8 Hz, 2H; 3-H, 9-H), 7.59 (d, *J* = 8.7 Hz, 4H; 2′-H), 7.65 (d, *J* = 1.8 Hz, 2H; 1-H, 7-H), 8.10–8.19 ppm (m, 2H; 4-H, 10-H); ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 26.1, 29.3, 29.4, 29.4, 29.6, 29.7, 29.7, 30.3, 31.9 (CH_2), 33.7 (C-6, C-12), 46.0 (C-6a, C-12a), 53.5 ($COOCH_3$), 68.1 (OCH_2), 114.8 (C-3′), 116.1 (C-4, C-10), 116.3 (C-1, C-7), 122.4 (C-3, C-9), 126.9 (C-6c, C-12c), 128.3 (C-2′), 128.3 (C-6b, C-12b), 134.0 (C-1′), 136.1 (C-2, C-8), 139.4 (C-4a, C-10a), 142.2 (C-5a, C-11a), 151.6 (NCOO), 158.5 ppm (C-4′); FT-IR (ATR): $\tilde{\nu}$ = 3038 (w), 2920 (s), 2851 (w), 1737 (w), 1603 (w), 1568 (w), 1516 (w), 1460 (s), 1442 (w), 1413 (w), 1366 (s), 1343 (s), 1305 (w), 1244 (s), 1217 (s), 1171 (s), 1122 (s), 1031 (w), 909 (w), 876 (w), 834 (w), 814 (w), 762 (w), 749 (w), 735 (w), 691 (w), 646 (w), 609 (w), 577 (w), 531 (w), 434 (w) cm^{-1}; MS (APCI): *m/z* = 921.57 $[M+H]^+$, 889.65 $[M-OCH_3+H]^+$, 863.56 $[M-COOCH_3+H]^+$, 663.45 $[M-CO_2CH_3+H]^+$, 576.43, 506.47, 448.28, 394.34, 333.17; HRMS (APCI): *m/z* calcd for $C_{60}H_{76}N_2O_6+H^+$: 921.5776 $[M+H]^+$, found: 921.5698 $[M+H]^+$.

Di-*tert*-butyl (6a*SR*,12a*SR*)-2,8-bis(4-dodecyloxyphenyl)-6,6a,12,12a-tetrahydropentale-no-[2,1-*b*:5,4-*b*′]diindole-5,11-dicarboxylate (Ph-**6g**): According to GP3, from **12c** (100 mg, 156 μmol), **10c** (354 mg, 623 μmol), K_2CO_3 (215 mg, 1.56 mmol), $Pd(PPh_3)_4$ (11.0 mg, 9.30 μmol); purification method A: chromatography with hexanes/EtOAc (50:1→10:1); yield: 71.0 mg, 70.6 μmol, 45 %, colorless solid, m.p.146 °C; ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.1 Hz, 6H; CH_3), 1.23–1.41 (m, 32H; CH_2), 1.45–1.51 (m, 4H; CH_2), 1.62 (s, 18H; BOC-CH_3), 1.79–1.86 (m, 4H; CH_2), 3.36–3.44 (m, 2H; 6-H_a, 12-H_a), 3.52–3.60 (m, 2H; 6-H_b, 12-H_b), 4.02 (t, *J* = 6.5 Hz, 4H; OCH_2), 4.44-4.50 (m, 2H; 6a-H, 12a-H), 6.99 (d, *J* = 8.4 Hz, 4H; 3′-H), 7.43 (dd, *J* = 8.5, 1.8 Hz, 2H; 3-H, 9-H), 7.58 (d, *J* = 8.4 Hz, 4H; 2′-H), 7.64 (d, *J* = 1.8 Hz, 2H; 1-H, 7-H), 8.08–8.16 ppm (m, 2H; 4-H, 10-H); ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 26.1 (CH_2), 28.2 (BOC-CH_3), 29.3, 29.4, 29.4, 29.6, 29.6, 29.7, 29.7, 31.9 (CH_2), 34.0 (C-6, C-12), 45.9 (C-6a, C-12a), 68.1 (OCH_2), 83.4 ($C(CH_3)_3$), 114.8 (C-3′), 116.2 (C-1, C-7), 116.2 (C-4, C-10), 122.2 (C-3, C-9), 126.4 (C-6b, C-12b), 126.5 (C-6c, C-12c), 128.2 (C-2′), 134.1 (C-1′), 135.8 (C-2, C-8), 139.4 (C-4a, C-10a), 142.7 (C-5a, C-11a), 149.8 (NCOO), 158.4 ppm (C-4′); FT-IR (ATR): $\tilde{\nu}$ = 2922 (w), 2852 (w), 1725 (s), 1606 (w), 1579 (w), 1516 (w), 1459 (s), 1420 (w), 1369 (s), 1331 (w), 1303 (w), 1294 (w), 1263 (w), 1250 (s), 1219 (w), 1170 (w), 1143 (w), 1119 (s), 1026 (w), 966 (w), 873 (w), 837 (w), 815 (w), 767 (w), 725 (w), 687 (w), 608 (w), 572 (w), 532 (w), 494 (w), 471 (w), 434 (w) cm^{-1}; MS (ESI): *m/z* = 1027.61 $[M+Na]^+$, 685.42, 663.44, 625.43, 597.40, 447.34, 393.29, 333.16; HRMS (ESI): *m/z* calcd for $C_{66}H_{88}N_2O_6+Na^+$: 1027.6535 $[M+Na]^+$, found: 1027.6483 $[M+Na]^+$; elemental analysis calcd (%) for $C_{66}H_{88}N_2O_6$: C 78.84, H 8.82, N 2.79; found: C 77.97, H 8.59, N 2.67.

Dibenzyl (6a*SR*,12a*SR*)-2,8-bis(4-dodecyloxyphenyl)-6,6a,12,12a-tetrahydropentaleno-[2,1-*b*:5,4-*b*′]diindole-5,11-dicarboxylate (Ph-**6h**): According to GP3, from **12d** (100 mg, 156 μmol), **10c** (172 mg, 563 μmol) K_2CO_3 (195 mg, 1.41 mmol), $Pd(PPh_3)_4$ (16.0 mg, 8.40 μmol), purification method A: chromatography with hexanes/EtOAc (50:1→5:1); yield: 15 mg, 13.9 μmol, 10 %, colorless solid, m.p. > 350 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.8 Hz, 6H; CH_3), 1.20–1.44 (m, 32H; CH_2), 1.45–1.55 (m, 4H; CH_2), 1.78–1.89 (m, 4H; CH_2), 3.27–3.39 (m, 2H; 6-H_a, 12-H_a), 3.41–3.52 (m, 2H; 6-H_b, 12-H_b), 4.04 (t, *J* = 6.6 Hz, 4H; OCH_2), 4.34–4.49 (m, 2H; 6a-H, 12a-H), 5.36 (s, 4H; $COOCH_2$), 7.01 (d, *J* = 8.7 Hz, 4H; 3′-H), 7.21–7.31 (m, 6H; 4″-H, 5″-H), 7.36–7.46 (m, 6H; 3-H, 9-H, 3″-H), 7.52–7.60 (m, 6H; 1-H, 7-H, 2′-H), 8.11–8.20 ppm (m, 2H; 4-H, 10-H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (CH_3), 22.7, 26.1, 29.4, 29.5, 29.6, 29.6, 29.7, 29.7, 29.7, 31.9 (CH_2), 33.8 (C-6, C-12), 46.0 (C-6a, C-12a), 68.2 (OCH_2), 68.5 (C-1″), 114.8 (C-3′), 116.1 (C-4, C-10), 116.3 (C-1, C-7), 122.5 (C-3, C-9), 126.6 (C-6c, C-12c), 127.0 (C-6b, C-12b), 128.3, 128.4, 128.6, 128.7 (C-2′, C-3″, C-4″, C-5″), 134.1 (C-1′), 135.0 (C-2″), 136.2 (C-2, C-8), 139.4 (C-4a, C-10a), 142.1 (C-5a, C-11a), 150.8 ($NCOOCH_2$), 158.5 ppm (C-4′); FT-IR (ATR): $\tilde{\nu}$ = 3064 (w), 3035 (w), 2922 (s), 2852 (s), 1729 (s), 1608 (w), 1516 (w), 1461 (s), 1402 (s), 1359 (s), 1335 (w), 1304 (w), 1248 (s), 1214 (s), 1181 (w), 1124 (s), 1028 (s), 908 (w), 874 (w), 814 (s), 761 (w), 750 (w), 729 (w), 694 (w), 665 (w), 625 (w), 609 (w), 582 (w), 531 (w), 496 (w), 456 (w), 446 (w), 434 (w), 409 (w) cm^{-1}; MS (APCI): *m/z* = 1073.63 $[M+H]^+$, 1029.64, 922.01, 874.47, 813.42 $[M-C_6H_4OC_{12}H_{25}+H]$, 769.43, 721.36, 663.45, 614.36, 570.37, 524.31, 480.32, 429.09, 354.15, 310.16, 264.10; HRMS (APCI): *m/z* calcd for $C_{72}H_{84}N_2O_6+H^+$: 1073.6402 $[M+H]^+$, found: 1073.6392 $[M+H]^+$.

(6a*SR*,12a*SR*)-2,8-Bis(4-dodecyloxyphenyl)-5,11-ditosyl-5,6,6a,11,12,12a-hexahydropentaleno[2,1-*b*:5,4-*b*′]diindole (Ph-**6i**): According to GP3, from **12e** (175 mg, 233 μmol), **10c** (286 mg,

933 μmol), K_2CO_3 (322 mg, 2.33 mmol), $Pd(PPh_3)_4$ (27.0 mg, 23.3 μmol), purification method A: chromatography with hexanes/EtOAc (50:1→CH_2Cl_2); yield: 41 mg, 36.8 μmol, 16%, colorless solid, m.p. 183 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.7 Hz, 6H; CH_3), 1.19–1.42 (m, 32H; CH_2), 1.42–1.53 (m, 4H; CH_2), 1.81 (d, *J* = 7.1 Hz, 4H; CH_2), 2.16 (s, 6H; 5″-H), 3.31–3.48 (m, 2H; 6-H_a, 12-H_a), 3.49–3.61 (m, 2H; 6-H_b, 12-H_b), 4.01 (t, *J* = 6.5 Hz, 4H; OCH_2), 4.35–4.48 (m, 2H; 6a-H, 12a-H), 6.79 (d, *J* = 8.1 Hz, 4H; 3″-H), 6.99 (d, *J* = 8.7 Hz, 4H; 3′-H), 7.42–7.49 (m, 6H; 2″-H, 3-H, 9-H), 7.55 (d, *J* = 8.7 Hz, 4H; 2′-H), 7.62 (d, *J* = 1.7 Hz, 2H; 1-H, 7-H), 8.02 ppm (d, *J* = 8.6 Hz, 2H; 4-H, 10-H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.1 (CH_3), 21.5 (C-5″), 22.7, 26.1, 29.3, 29.4, 29.4, 29.6, 29.6, 29.6, 29.7, 31.9 (CH_2), 32.6 (C-6, C-12), 46.4 (C-6a, C-12a), 68.1 (OCH_2), 114.8 (C-4, C-10), 114.8 (C-3′), 116.7 (C-1, C-7), 122.6 (C-3, C-9), 126.2 (C-2″), 127.0 (C-2, C-8), 127.9 (C-6b, C-12b), 128.3 (C-2′), 129.6 (C-3″), 133.5 (C-1′), 135.3 (C-1″), 136.9 (C-6c, C-12c), 139.4 (C-4a, C-10a), 142.5 (C-5a, C-11a), 144.5 (C-4″), 158.7 ppm (C-4′); FT-IR (ATR): $\tilde{\nu}$ = 2918 (w), 2851 (w), 1606 (w), 1515 (w), 1453 (w), 1363 (s), 1332 (w), 1300 (w), 1274 (w), 1239 (w), 1206 (w), 1186 (w), 1167 (s), 1132 (w), 1117 (w), 1099 (w), 1087 (w), 1030 (w), 1016 (w), 1003 (w), 973 (w), 944 (w), 907 (w), 835 (w), 812 (s), 752 (w), 721 (w), 701 (w), 669 (s), 637 (w), 623 (w), 607 (w), 581 (s), 542 (s), 488 (w), 431 (w), 420 (w) cm^{-1}; MS (MALDI-TOF): *m/z* calcd for $C_{70}H_{84}N_2O_6S_2^+$: 1112.5 $[M]^+$, found: 1111.2 $[M]^+$.

Diethyl (6a*SR*,12a*SR*)-2,8-bis[3,4-bis(dodecyloxy)phenyl]-6,6a,12,12a-tetra-hydropentaleno[2,1-*b*:5,4-b′]diindole-5,11-dicarboxylate (Ph-**6l**): According to GP3, from **12a** (75.0 mg, 128 μmol), 3,4-bis(dodecyloxy)phenylboronic acid[17] (188 mg, 384 μmol), K_2CO_3 (53.0 mg, 384 μmol), $Pd(PPh_3)_4$ (15.0 mg, 12.8 μmol), purification method A: chromatography with hexanes/EtOAc (50:1→10:1); yield: 86.0 mg, 65.2 μmol, 51%, colorless solid, m.p. 168 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.84–0.92 (m, 12H; CH_3), 1.21–1.40 (m, 64H; CH_2), 1.43 (t, *J* = 7.2 Hz, 6H; $COOCH_2CH_3$), 1.45–1.55 (m, 8H; CH_2), 1.80-1.91 (m, 8H; CH_2), 3.35–3.43 (m, 2H; 6-H_a, 12-H_a), 3.51–3.61 (m, 2H; 6-H_b, 12-H_b), 4.06 (t, *J* = 6.6 Hz, 4H; OCH_2), 4.10 (t, *J* = 6.6 Hz, 4H; OCH_2), 4.36–4.48 (m, 4H; $COOCH_2$), 4.48–4.53 (m, 2H; 6a-H, 12a-H), 6.98 (d, *J* = 8.0 Hz, 2H; 5′-H), 7.16–7.22 (m, 4H; 2′-H, 6′-H), 7.44 (dd, *J* = 8.6, 1.8 Hz, 2H; 3-H, 9-H), 7.64 (d, *J* = 1.8 Hz, 2H; 1-H, 7-H), 8.16 ppm (d, *J* = 8.6 Hz, 2H; 4-H, 10-H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (CH_3), 14.5 ($COOCH_2CH_3$), 22.7, 26.1, 26.1, 29.4, 29.4, 29.5, 29.5, 29.7, 29.7, 29.7, 31.9 (CH_2), 33.9 (C-6a, C-12a), 46.0 (C-6, C-12), 62.9 ($COOCH_2$), 69.5 (OCH_2), 69.6 (OCH_2), 113.7 (C-6′), 114.3 (C-5′), 116.1 (C-4, C-10), 116.4 (C-1, C-7), 119.9 (C-2′), 122.6 (C-3, C-9), 126.5 (C-6b, C-12b), 126.8 (C-6c, C-12c), 134.9 (C-1′), 136.3 (C-2, C-8), 139.5 (C-4a, C-10a), 142.4 (C-5a, C-11a), 148.7 (C-3′), 149.4 (C-4′), 151.1 ppm (NCOO); FT-IR (ATR): $\tilde{\nu}$ = 2921 (s), 2852 (s), 1732 (s), 1614 (w), 1584 (w), 1519 (w), 1462 (s), 1425 (w), 1406 (w), 1380 (w), 1351 (w), 1329 (w), 1252 (s), 1217 (w), 1199 (w), 1146 (w), 1124 (s), 1037 (w), 853 (w), 807 (w), 763 (w), 722 (w) cm^{-1}; MS (ESI): *m/z* = 1340 $[M + Na]^+$; HRMS (ESI): *m/z* calcd for $C_{86}H_{128}N_2O_8 + Na^+$: 1339.9563 $[M + Na]^+$, found: 1339.9490 $[M + Na]^+$.

Diethyl (6a*SR*,12a*SR*)2,8-bis[3,4,5-tris(dodecyloxy)phenyl]-6,6a,12,12a-tetrahydropentaleno[2,1-b:5,4-*b*′]diindole-5,11-dicarboxylate (Ph-**6m**): According to GP3, from **12a** (100 mg, 171 μmol), 3,4,5-tris(dodecyloxy)phenylboronic acid[18] (288 mg, 426 μmol), K_2CO_3 (71.0 mg, 512 μmol), $Pd(PPh_3)_4$ (20.0 mg, 17.1 μmol), purification method A: chromatography with hexanes/EtOAc (50:1→1:1); yield: 125 mg, 74.1 μmol, 43%, colorless solid, m.p. 77 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.85–0.91 (m, 18H; CH_3), 1.20–1.39 (m, 108H; CH_2), 1.43 (t, *J* = 7.1 Hz, 6H; $COOCH_2CH_3$), 1.47–1.56 (m, 12H; CH_2), 3.36–3.43 (m, 2H; 6-H_a, 12-H_a), 3.53–3.63 (m, 2H; 6-H_b, 12-H_b), 4.02 (t, *J* = 6.6 Hz, 4H; *p*-OCH_2), 4.05–4.12 (m, 8H; *m*-OCH_2), 4.36–4.48 (m, 4H; $COOCH_2$), 4.48–4.53 (m, 2H; 6a-H, 12a-H), 6.83 (s, 4H; 2′-H), 7.44 (dd, *J* = 8.6, 1.8 Hz, 2H; 3-H, 9H), 7.63 (d, *J* = 1.8 Hz, 2H; 1-H, 7-H), 8.17 ppm (d, *J* = 8.6 Hz, 2H; 4-H, 10-H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (CH_3), 14.4 ($CO_2CH_2CH_3$), 22.7, 22.7, 26.2, 26.2, 29.4, 29.4, 29.5, 29.6, 29.7, 29.7, 29.7, 29.8, 29.8, 30.4, 31.9, 32.0 (CH_2), 33.9 (C-6, C-12), 46.0 (C-6a, C-12a), 62.9 ($COOCH_2$), 69.4 (m-OCH_2), 73.6 (*p*-OCH_2), 106.5 (C-2′), 116.1 (C-4, C-10), 116.6 (C-1, C-7), 122.8 (C-3, C-9), 126.5 (C-6b, C-12b), 126.8 (C-6c, C-12c), 136.7 (C-2, C-8), 137.2 (C-1′), 137.8 (C-4′), 139.7 (C-4a, C-10a), 142.4 (C-5a, C-11a), 151.1 (NCOO), 153.4 ppm (C-3′); FT-IR (ATR): $\tilde{\nu}$ = 2921 (s), 2852 (w), 1736 (w), 1583 (w), 1566 (w), 1508 (w), 1458 (s), 1424 (w), 1377 (w), 1336 (w), 1258 (w), 1216 (w), 1116 (s), 1041 (w), 907 (s), 814 (w), 764 (w), 731 (s), 641 (w), 584 (w), 496 (w) cm^{-1}; MS (ESI): *m/z* = 1709 $[M + Na]^+$; HRMS (ESI): *m/z* calcd for $C_{110}H_{176}N_2O_{10} + Na^+$: 1708.3217 $[M + Na]^+$, found: 1708.3174 $[M + Na]^+$.

Diethyl (6a*SR*,12a*SR*)-2,8-bis(4′-(decyloxy)-[1,1′-biphenyl]-4-yl)-6,6a,12,12a-tetrahydropentaleno[2,1-*b*:5,4-*b*′]diindole-5,11-dicarboxylate (Biph-**6a**): According to GP3, from **12a** (250 mg, 426 μmol), 4′-(decyloxy)-4-biphenylboronic acid[24a] (553 mg, 1.28 mmol), K_2CO_3 (117 mg, 1.28 mmol), $Pd(PPh_3)_4$ (49.0 mg, 42.6 μmol), purification method B and subsequent recrystallization from CH_2Cl_2; yield: 101 mg, 96.6 μmol, 23%, colorless solid; ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.0 Hz, 6H; CH_3), 1.23–1.40 (m, 24H; CH_2), 1.43 (t, *J* = 7.1 Hz, 6H; $COOCH_2CH_3$), 1.45–1.51 (m, 4H; CH_2), 1.78–1.85 (m, 4H; CH_2), 3.36–3.44 (m, 2H; 6-H_a, 12-H_a), 3.53–3.61 (m, 2H; 6-H_b, 12-H_b), 4.00 (t, *J* = 6.5 Hz, 4H; OCH_2), 4.34–4.49 (m, 4H; $COOCH_2$), 4.47-4.54 (m, 2H; 6a-H, 12a-H), 6.99 (d, *J* = 8.6 Hz, 4H; 7′-H), 7.52 (dd, *J* = 8.5, 1.9 Hz, 2H; 3-H, 9-H), 7.58 (d, *J* = 8.6 Hz, 4H; 6′-H), 7.65 (d, *J* = 8.3 Hz, 4H; 3′-H), 7.72 (d, *J* = 8.3 Hz, 4H; 2′-H), 7.74 (d, *J* = 1.9 Hz, 2H; 1-H, 7-H), 8.15–8.25 ppm (m, 2H; 4-H, 10-H); ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.2 (CH_3), 14.5 ($CO_2CH_2CH_3$), 22.7, 26.1, 29.3, 29.3, 29.4, 29.6, 29.6, 31.9 (CH_2), 33.8 (C-6, C-12), 46.0 (C-6a, C-12a), 62.9 ($COOCH_2$), 68.1 (OCH_2), 114.8 (C-7′), 116.2 (C-4, C-10), 116.5 (C-1, C-7), 122.5 (C-3, C-9), 126.6 (C-6b, C-12b), 126.8 (C-6c, C-12c), 127.0 (C-3), 127.6 (C-2′), 128.0 (C-6′), 133.0 (C-5′), 135.8 (C-2, C-8), 139.4 (C-4′), 139.8 (C-4a, C-10a), 139.9 (C-1′), 142.4 (C-5a, C-11a), 151.1 (NCOO), 158.7 ppm (C-8′); FT-IR (ATR): $\tilde{\nu}$ = 2920 (w), 2850 (w), 1728 (s), 1605 (w), 1501 (w), 1458 (s), 1405 (w), 1375 (s), 1352 (w), 1325 (s), 1242 (s), 1213 (s), 1176 (w), 1117 (s), 1046 (w), 815 (s), 766 (w), 704 (w), 524 (w) cm^{-1}; MS (MALDI-TOF): *m/z* calcd for $C_{70}H_{80}N_2O_6^+$: 1440.6, found: 1042.1; elemental analysis calcd (%) for $C_{70}H_{80}N_2O_6$: C 80.42, H 7.72, N 2.68; found: C 80.06, H 7.59, N 2.66. DSC: 203 °C (30.2 kJ mol^{-1}) N 338 °C I (decomp., 1. heating).

Diethyl (6a*SR*,12a*SR*)-2,8-bis(4′-(dodecyloxy)-[1,1′-biphenyl]-4-yl)-6,6a,12,12a-tetrahydropentaleno[2,1-*b*:5,4-*b*′]diindole-5,11-dicarboxylate (Biph-**6b**): According to GP3, from **12a** (100 mg, 170 μmol), 4′-(dodecyloxy)-4-biphenylboronic acid[24b] (196 mg, 512 μmol), K_2CO_3 (71.0 mg, 512 μmol), $Pd(PPh_3)_4$ (20.0 mg, 17.1 μmol), purification method B; yield: 55 mg, 49.9 μmol, 29%, colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 6.9 Hz, 6H; CH_3), 1.21–1.41 (m, 32H; CH_2), 1.43 (t, *J* = 7.1 Hz, 6H; $COOCH_2CH_3$), 1.46–1.52 (m, 4H; CH_2), 1.76–1.88 (m, 4H; CH_2), 3.38–3.45 (m, 2H; 6-H_a, 12-H_a), 3.55-3.64 (m, 2H; 6-H_b, 12-H_b), 4.01 (t, *J* = 6.6 Hz, 4H; OCH_2), 4.36–4.49 (m, 4H; $COOCH_2$), 4.49–4.55 (m, 2H; 6a-H, 12a-H), 7.00 (d, *J* = 9.6 Hz, 4H; 7′-H), 7.53 (dd, *J* = 8.6, 1.9 Hz, 2H; 3-H, 9-H), 7.59 (d, *J* = 9.6 Hz, 4H; 6′-H), 7.66 (d, *J* = 8.4 Hz, 4H; 3′-H), 7.73 (d, *J* = 8.4 Hz, 4H; 2′-H), 7.75 (d, *J* = 1.9 Hz, 2H; 1-H, 7-H), 8.20 ppm (d, *J* = 8.6 Hz, 2H; 4-H, 10-H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.1 (CH_3), 14.5 ($COOCH_2CH_3$), 22.7, 26.1, 29.3, 29.4, 29.4, 29.6, 29.6, 29.7, 29.7, 31.9 (CH_2), 33.9 (C-6, C-12), 46.0 (C-6a, C-12a), 62.9 ($COOCH_2$), 68.1 (OCH_2), 114.9 (C-7′), 116.2 (C-4, C-10), 116.6 (C-1, C-7), 122.6 (C-3, C-9), 126.6 (C-6b, C-12b), 126.9 (C-6c, C-12c), 127.0 (C-3′), 127.7 (C-2′), 128.0 (C-6′), 133.0 (C-5′), 135.9 (C-2, C-8), 139.5 (C-4′), 139.8 (C-4a, C-10a), 140.0 (C-1′), 142.6 (C-5a, C-11a), 151.1 (NCOO), 158.8 ppm (C-8′); FT-IR (ATR): $\tilde{\nu}$ = 2922 (s), 2852 (w), 1735 (s), 1609 (w), 1580 (w), 1529 (w), 1503 (w), 1461 (s), 1406 (w), 1379 (s), 1352 (w), 1332 (w), 1284 (w), 1249 (s), 1216 (w), 1204 (w), 1178 (w), 1123 (s), 1051 (w), 999 (w), 878 (w), 813 (s), 764 (w), 705 (w), 621 (w), 519 (w) cm^{-1}; MS (MALDI-TOF): *m/z* calcd for $C_{74}H_{88}N_2O_6^+$: 1100.6, found: 1098.2; elemental analysis calcd (%)

for $C_{74}H_{88}N_2O_6$: C 80.69, H 8.05, N 2.54; found: C 79.97, H 7.78, N 2.47. DSC: 193 °C (30.2 kJ mol^{-1}) SmA 207 °C (60.1 kJ mol^{-1}) N 303 °C I (decomp., 1. heating).

Diethyl (6a*SR*,12a*SR*)-2,8-bis(4′-(tetradecyloxy)-[1,1′-biphenyl]-4-yl)-6,6a,12,12a-tetrahydropentaleno[2,1-*b*:5,4-*b*′]diindole-5,11-dicarboxylate (Biph-**6c**): According to GP3, from **12a** (250 mg, 426 μmol), 4′-(tetradecyloxy)-4-biphenylboronic acid[24c] (525 mg, 1.28 mmol), K_2CO_3 (117 mg, 1.28 mmol), $Pd(PPh_3)_4$ (49.0 mg, 42.6 μmol), purification method B; yield: 213 mg, 184 μmol, 43 %, colorless solid; ^{1}H NMR (700 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.0 Hz, 6H; C*H*$_3$), 1.23–1.40 (m, 40H; C*H*$_2$), 1.43 (t, *J* = 7.1 Hz, 6H; $CO_2CH_2CH_3$), 1.45–1.52 (m, 4H; C*H*$_2$), 1.77–1.86 (m, 4H; C*H*$_2$), 3.36–3.46 (m, 2H; 6-H$_a$, 12-H$_a$), 3.51–3.64 (m, 2H; 6-H$_b$, 12-H$_b$), 4.01 (t, *J* = 6.5 Hz, 4H; OC*H*$_2$), 4.3–4.48 (m, 4H; COOC*H*$_2$), 4.49–4.52 (m, 2H; 6a-H, 12a-H), 6.99 (d, *J* = 8.6 Hz, 4H; 7′-H), 7.53 (dd, *J* = 8.5, 1.9 Hz, 2H; 3-H, 9-H), 7.58 (d, *J* = 8.6 Hz, 4H; 6′-H), 7.66 (d, *J* = 8.2 Hz, 4H; 3′-H), 7.73 (d, *J* = 8.2 Hz, 4H; 2′-H), 7.74 (d, *J* = 1.9 Hz, 2H; 1-H, 7-H), 8.17–8.22 ppm (m, 2H; 4-H, 10-H); ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.1 (*C*H$_3$), 14.5 ($COOCH_2CH_3$), 22.7, 26.1, 29.3, 29.4, 29.4, 29.6, 29.6, 29.7, 29.7, 29.7, 29.7, 31.9 (*C*H$_2$), 33.9 (C-6, C-12), 46.0 (C-6a, C-12a), 62.9 (COO*C*H$_2$), 68.1 (O*C*H$_2$), 114.8 (C-7′), 116.2 (C-4, C-10), 116.6 (C-1, C-7), 122.6 (C-3, C-9), 126.6 (C-6b, C-12b), 126.8 (C-6c, C-12c), 127.0 (C-3′), 127.6 (C-2′), 128.0 (C-6′), 133.0 (C-5′), 135.9 (C-2, C-8), 139.4 (C-4′), 139.8 (C-4a, C-10a), 139.9 (C-1′), 142.5 (C-5a, C-11a), 151.1 (NCOO), 158.8 ppm (C-8′); FT-IR (ATR): $\tilde{\nu}$ = 2917 (w), 2848 (w), 1728 (w), 1605 (w), 1501 (w), 1457 (s), 1403 (w), 1375 (w), 1353 (w), 1326 (s), 1267 (w), 1242 (s), 1213 (w), 1196 (w), 1175 (w), 1118 (s), 1032 (w), 998 (w), 815 (s), 766 (w), 723 (w), 704 (w), 669 (w), 524 (w), 432 (w) cm^{-1}; MS (MALDI-TOF): *m/z* calcd for $C_{78}H_{96}N_2O_6^+$: 1156.72, found: 1155.1; elemental analysis calcd (%) for $C_{78}H_{96}N_2O_6$: C 80.93, H 8.36, N 2.42; found: C 80.80, H 8.20, N 2.30. DSC: 168 °C (16.3 kJ mol^{-1}) SmA 193 °C (33.9 kJ mol^{-1}) N 301 °C I (decomp., 1. heating).

Diethyl (6a*SR*,12a*SR*)-2,8-bis(4′-(hexadecyloxy)-[1,1′-biphenyl]-4-yl)-6,6a,12,12a-tetrahydropentaleno[2,1-*b*:5,4-*b*′]diindole-5,11-dicarboxylate (Biph-**6d**): According to GP3, from **12a** (250 mg, 426 μmol), 4′-(hexadecyloxy)-4-biphenylboronic acid[24c] (561 mg, 1.28 mmol), K_2CO_3 (117 mg, 1.28 mmol), $Pd(PPh_3)_4$ (49.0 mg, 42.6 μmol), purification method B; yield: 120 mg, 98.9 μmol, 23 %, colorless solid; ^{1}H-NMR (700 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.1 Hz, 6H; C*H*$_3$), 1.22–1.41 (m, 40H; C*H*$_2$), 1.44 (t, *J* = 7.1 Hz, 6H; $COOCH_2CH_3$), 1.46–1.52 (m, 4H; C*H*$_2$), 1.78–1.87 (m, 4H; C*H*$_2$), 3.39–3.46 (m, 2H; 6-H$_a$, 12-H$_a$), 3.56–3.63 (m, 2H; 6-H$_b$, 12-H$_b$), 4.02 (t, *J* = 6.6 Hz, 4H; OC*H*$_2$), 4.38–4.50 (m, 4H; COOC*H*$_2$), 4.50–4.56 (m, 2H; 6a-H, 12a-H), 7.00 (d, *J* = 8.7 Hz, 4H; 7″-H), 7.54 (dd, *J* = 8.6, 1.8 Hz, 2H; 3-H, 9-H), 7.60 (d, *J* = 8.7 Hz, 4H; 6″-H), 7.67 (d, *J* = 8.2 Hz, 4H; 3″-H), 7.72–7.77 (m, 6H; 1-H, 7-H, 2″-H), 8.18–8.24 ppm (m, 2H; 4-H, 10-H); ^{13}C NMR (176 MHz, $CDCl_3$): δ = 14.2 (*C*H$_3$), 14.5 ($COOCH_2CH_3$), 22.7, 26.1, 29.3, 29.4, 29.4, 29.6, 29.7, 29.7 (*C*H$_2$), 31.9 (C-6, C-12), 46.0 (C-6a, C-12a), 62.9 (COO*C*H$_2$), 68.1 (O*C*H$_2$), 114.8 (C-7′), 116.2 (C-4, C-10), 116.6 (C-1, C-7), 122.6 (C-3, C-9), 126.6, 126.6 (C-1′, C-6b, C-12b), 127.0, 127.7, 128.0 (C-2′, C-3′, C-6′), 133.0 (C-5′), 135.9 (C-2, C-8), 139.4 (C-4′), 139.8 (C-4a, C-10a), 139.9 (C-6, C-12c), 140.2 (C-5a, C-11a), 151.1 (NCOO), 158.8 ppm (C-8′); FT-IR (ATR): $\tilde{\nu}$ = 2919 (s), 2849 (w), 1730 (s), 1607 (w), 1502 (w), 1459 (s), 1405 (w), 1377 (s), 1353 (w), 1327 (s), 1270 (w), 1245 (s), 1214 (w), 1177 (w), 1120 (s), 1048 (w), 816 (s), 766 (w), 724 (w), 704 (w), 525 (w) cm^{-1}; MS (MALDI-TOF): *m/z* calcd for $C_{82}H_{104}N_2O_6^+$: 1212.78, found: 1209.9; elemental analysis calcd (%) for $C_{82}H_{104}N_2O_6$: C 81.15, H 8.64, N 2.31; found: C 81.25, H 8.41, N 2.41. DSC: 154 °C (19.2 kJ mol^{-1}) SmA 196 °C (29.3 kJ mol^{-1}) N 304 °C I (decomp., 1. heating).

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Conflict of Interest

The authors declare no conflict of interest.

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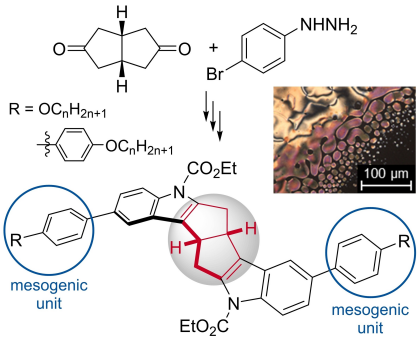
The indole-containing *concave*-shaped calamitic liquid crystals, accessible from Weiss diketone and bromophenylhydrazine in three steps involving Fischer indole, *N*-protection, and Suzuki cross-coupling, formed N and SmA mesophases whose range and type depended on the substituent R.



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