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Supporting Information

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Supramolecular Liquid Crystals Based on Cyclo[8]pyrrole –

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Instrumentation and methods. Proton, ^{13}C, and two-dimensional NMR spectra were measured on Varian Unity Plus (300 MHz for ^{1}H), Varian Mercury (400 MHz), and Bruker Avance spectrometers (500 MHz). Unless noted otherwise, all spectra were recorded at room temperature. Gradient-selected ^{1}H-^{13}C correlation spectra were recorded with a resolution of 1024 to 2048 in the t_1 domain. Chemical shifts were referenced to residual solvent signals (7.24 ppm for $C^{1}HCl_3$ in $CDCl_3$, 77.0 ppm for $^{13}CDCl_3$). High-resolution chemical ionization (CI) mass spectra were obtained on a Waters (Micromass) Autospec mass spectrometer and the low-resolution electrospray ionization (ESI) spectrum was obtained on a Finnigan LCQ Classic mass spectrometer. Electronic spectra were obtained on a Cary 5000 UV-vis-NIR spectrophotometer (courtesy of the Center for Nano- and Molecular Science and Technology at UT Austin). Elemental analyses were carried out at Midwest Microlab, Indianapolis, IN (USA). DSC data (30 to 220 °C, 10 deg/min.) were collected using a Perkin Elmer DSC 7 calorimeter. Samples were crimped in airtight pans to reduce the loss of TNB on heating. Optical microscopy observations were carried out using an Olympus BX41 polarizing microscope equipped with a hot stage (Instec Inc., model HCS402) and a 4 megapixel CCD camera. Color balance, tonal range, and sharpness were uniformly adjusted using standard methods. Brightness levels were measured using the spot-metering feature of the camera. Films of C8P were spread mechanically at 100 °C using a sharp razor. The average thickness of the films was estimated from their electronic absorption spectra using the extinction coefficients obtained for C8P solutions.

XRD analysis. The XRD patterns were obtained with two different experimental set-ups. In all cases, a linear monochromatic Cu-Kα_1 beam (λ = 1.5405 Å) was obtained using a sealed-tube generator (900 W) equipped with a bent quartz monochromator. In the first set, the transmission Guinier geometry was used, whereas a Debye-Scherrer-like geometry was used in the second experimental set-up. In all cases, the crude powder was filled in Lindemann capillaries of 1 mm diameter and 10 μm wall thickness. An initial set of diffraction patterns was recorded on an image plate; periodicities up to 80 Å can be measured, and the sample temperature controlled to within ± 0.3 °C from 20 to 350 °C. The second set of diffraction patterns was recorded with a curved Inel CPS 120 counter gas-filled detector linked to a data acquisition computer; periodicities up to 60 Å can be measured, and the sample temperature controlled to within ± 0.05 °C from 20 to 200 °C. In each case, exposure times were varied from 1 to 24 h.

Volume calculation.[1-3] The volumes, V, of cyclopyrrole adducts were estimated using the formula

$$V = \frac{M}{\lambda \rho N_A},$$

where M is the molecular weight of the donor-acceptor pair, N_A is the Avogadro number, ρ is the volume mass (~ 1 g/cm^3), and $\lambda(T)$ is a temperature correction coefficient at the temperature of experiment (T). It is defined as

$$\lambda = \frac{V_{CH_2}(T^0)}{V_{CH_2}(T)},$$

where

$$V_{CH_2}(T) = 26.5616 + 0.02023 \cdot T$$

is the volume of a methylene group (in Å^3) at a given temperature (in °C), and T^0 = 25 °C. (The temperature variation of molecular volume of the complex is expected to follow the trend determined experimentally for the methylene group). The intracolumnar repeating distance h is calculated directly from the estimated molecular volume according to

$$h = \frac{NV}{S},$$

in which N is the number of molecules (aggregation number) within this fraction of column (here N is chosen equal to 1 as the molecule is disc-like), and S is the lattice area (columnar cross-section). For a hexagonal lattice

$$S = a^2 \frac{\sqrt{3}}{2},$$

where

$$a = \frac{2d_{10}}{\sqrt{3}}$$

is the lattice parameter obtained from the XRD analysis.

Table S1. XRD data for the Col_h phases studied. Symbols used: VS very strong, S strong, Br broad, Sh sharp.

Compounds	d_{meas}/Å	Intensity	Indexation *hk*	d_{calc}/Å	Parameters
1a·TNF	21.85	VS	10	21.8	a = 25.15 Å
	12.56	S	11	12.6	S = 550.0 Å^2
	7.2-7.3	Br	h_2		
	4.6	Br	h_{ch}		
	3.6	Sh	h_0		
1b·TNB	26.9	VS	10	27.0	a = 31.15 Å
	15.7	S	11	15.6	S = 840.0 Å^2
	5.7	Br	h_1		
	4.8	Br	h_{ch}		
	3.6	Br	h_0		
1b·TNP	27.4	VS	10	27.4	a = 31.65 Å
	5.5	Br	h_1		S = 870.0 Å^2
	4.8	Br	h_{ch}		
	3.7	Br	h_0		
1c·TNB	29.4	VS	10	29.4	a = 33.95 Å
	16.95	S	11	17.0	S = 1000.0 Å^2
	4.55	Br	h_{ch}		
	3.6	Br	h_0		

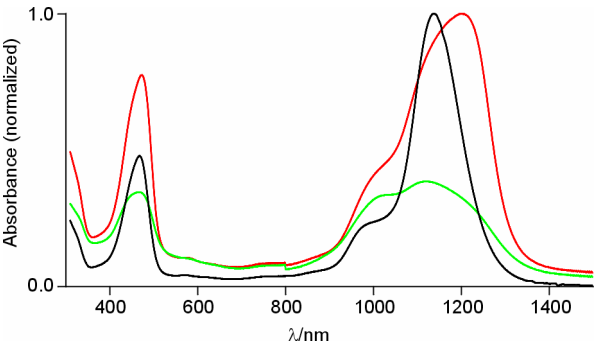


Figure S1. UV-vis-NIR electronic absorption spectra of **1c**: solution spectrum (CH_2Cl_2, black line), thin film (red line), and the same thin film after exposure to TNT vapors (green line).

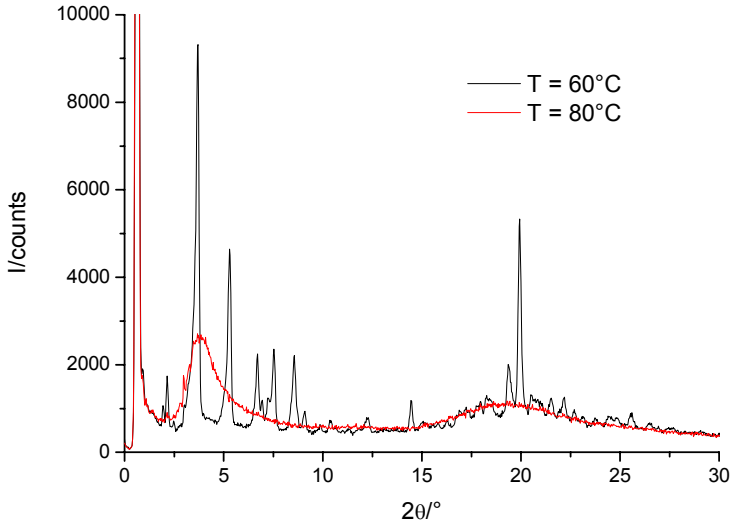


Figure S2. Powder X-ray diffractograms for **1a**.

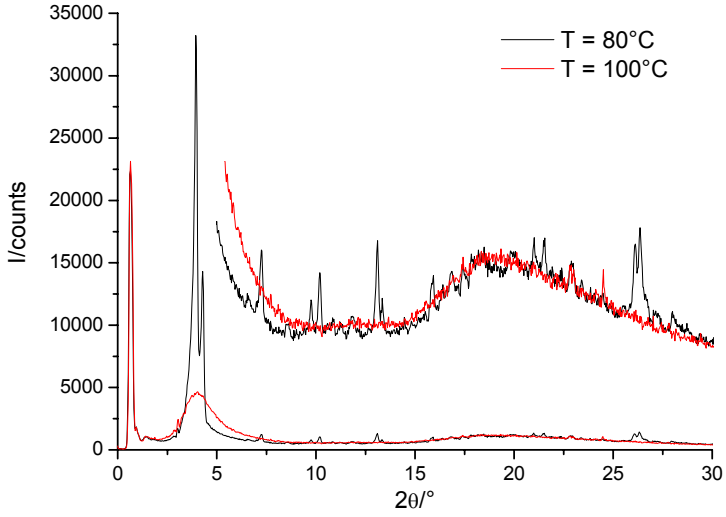


Figure S3. Powder X-ray diffractograms for **1a**·2TNB.

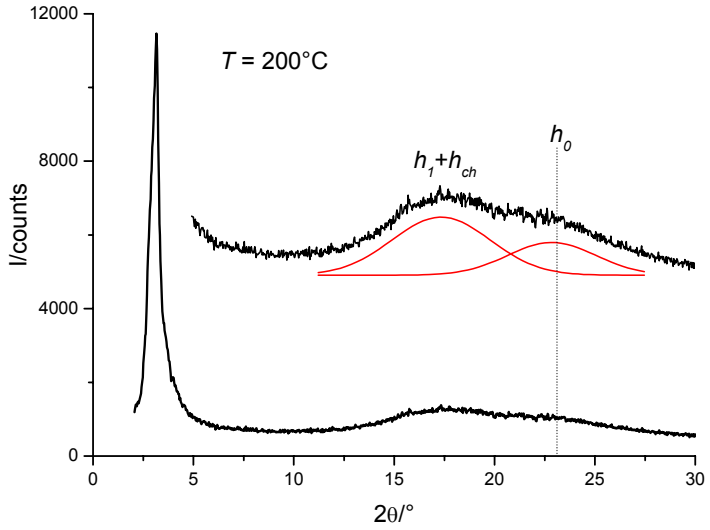


Figure S4. Powder X-ray diffractograms for **1b**·TNP.

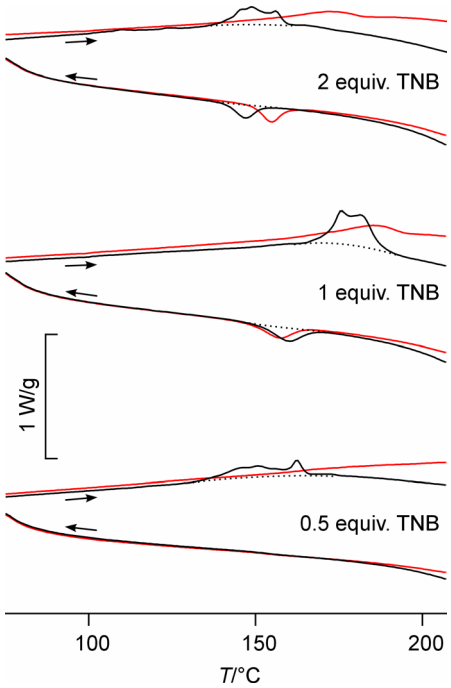


Figure S5. DSC traces (10 deg/min) obtained for samples of **1c** containing varying amounts of TNB (0.5, 1, and 2 equivalents). First heating and cooling scans (black lines) are shown for each stoichiometry and reveal features consistent with a single LC to isotropic liquid transition. Multiple peaks observed on the heating curves are due to the initially non-uniform packing of the samples in DSC pans. On further heating (second heat-cool cycles, red lines), the peaks shift as a result of partial loss of TNB from the sample. For 2 equivalents, the shift is towards higher temperatures, for the 1 equiv. sample the shift is to lower temperatures. For the 0.5 equiv. sample, the peaks disappear totally.

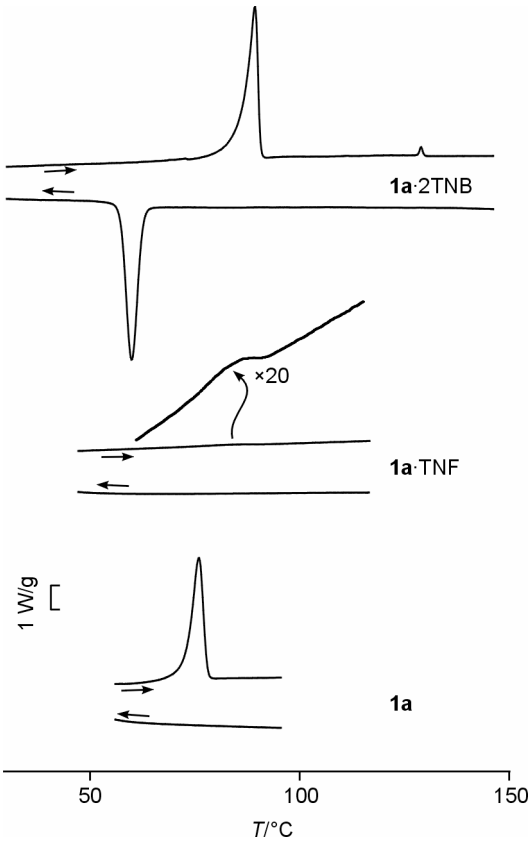


Figure S6. DSC traces (10 deg/min, first heat/cool cycles) obtained for samples of **1a**, **1a**·TNF, and **1a**·2TNB. No crystallization was observed for **1a** on cooling. For **1a**·TNF a vertical expansion is included to show the clearing transition. The small peak at ca. 130 °C in the **1a**·2TNB trace, corresponds to melting of excess TNB.

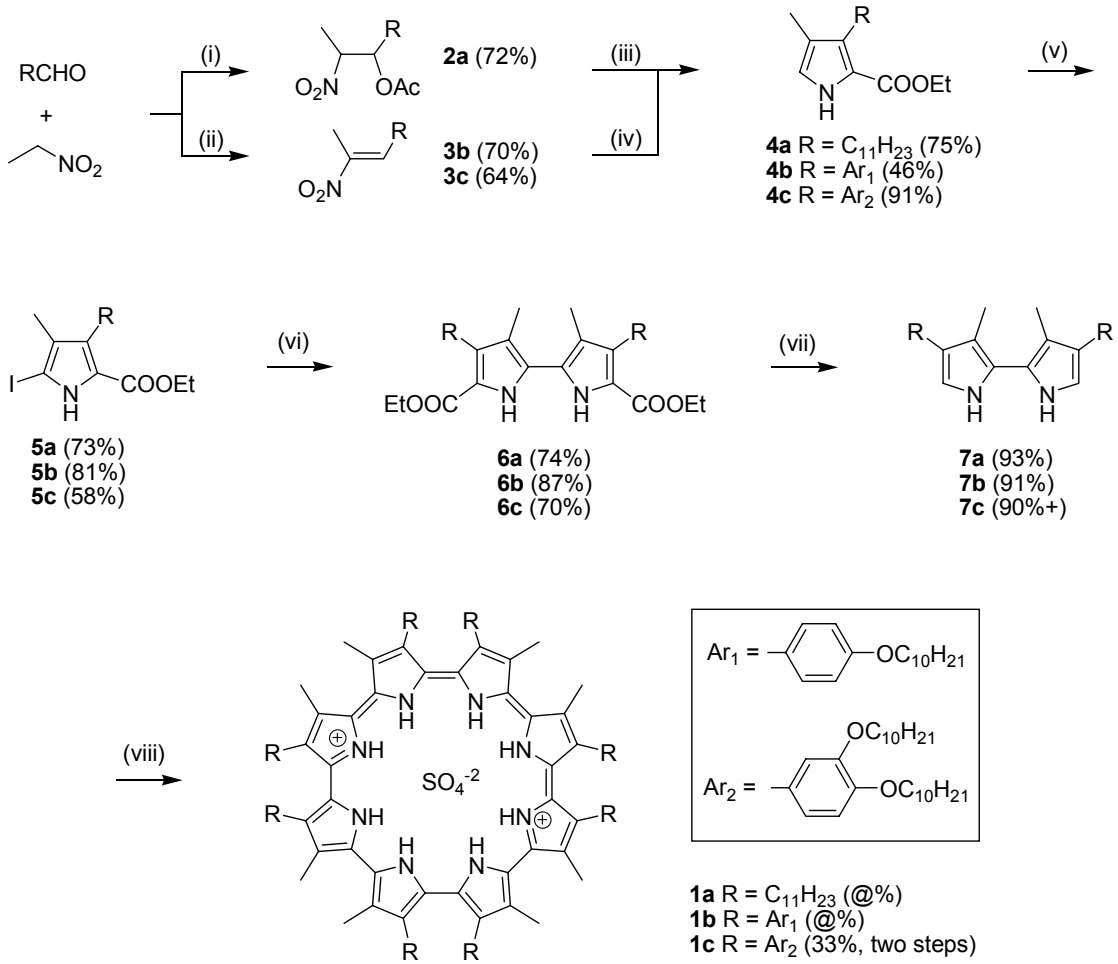
Compound	melting point /°C
TNF	176
TNB	123
TNT	82
TNP	122

Table S2. Literature melting points of electron acceptors used.

Syntheses

General. Ethyl isocyanoacetate (Fluka), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, Acros), di-*t*-butyl dicarbonate (Acros), copper (99.7%, dendritic 3 μm, Aldrich), 4-(dimethylamino)pyridine (DMAP, Aldrich), 2,4,6-trinitrotoluene (TNT, Chem Service), 1,3,5-trinitrobenzene (TNB, Chem Service), and other chemicals were obtained commercially and used as received. Tetrahydrofuran and toluene were dried by passing through activated alumina columns. Other solvents were reagent grade and used as received. Unless noted otherwise, TLC analyses were performed on analytical silica plates with a fluorescent indicator (Whatman) using 10% ethyl acetate in hexanes as the mobile phase.

WARNING: 2,4,6-Trinitrotoluene (TNT), 1,3,5-trinitrobenzene (TNB), and 2,4,6-trinitrophenol (picric acid, TNP) are known explosives and should be handled by qualified persons using appropriate protective equipment. In the experiments presented herein no explosion was ever observed even when these materials were heated. It is, however, strongly recommended that these potential explosives be used only in very small quantities, as was the case in all the studies reported herein.



Scheme S1. Synthesis of cyclo[8]pyrroles **1a-c**. Conditions: (i) 1. THF/DBU, 2. Ac_2O, CH_2Cl_2, DMAP; (ii) $AcONH_4$; (iii) $CNCH_2COOEt$, THF/*i*-PrOH, K_2CO_3; (iv) $CNCH_2COOEt$, THF/*i*-PrOH, DBU; (v) I_2,

NaI, $NaHCO_3$, DCE, H_2O, Δ; (vi) 1. Boc_2O, DMAP, CH_2Cl_2, 2. Cu, toluene, Δ, 3. 180 °C, vacuum; (vii) KOH, glycol, 200 °C; (viii) $FeCl_3$, H_2SO_4 (1M), CH_2Cl_2.

2-Nitrotetradecan-3-yl acetate (2a). Nitroethane (10.1 g, 0.135 mol) and dodecanal (24.9 g, 0.135 mol) were dissolved in THF (175 mL). DBU (4.11 g, 0.2 equiv.) was added dropwise and the reaction mixture was stirred overnight. dichloromethane (175 mL) was subsequently added and the solution was washed twice with 1M HCl and once with H_2O. The organic phase was dried with Na_2SO_4 and filtered. Acetic anhydride (35 mL, excess) was added followed by DMAP (1.32 g, 0.08 equiv.). After 15 minutes of stirring methanol (35 mL) was slowly added to quench the reaction. Saturated $NaHCO_3$ was added to decompose excess anhydride, the organic layer was separated, and the aqueous layer was extracted with dichloromethane. The organic fractions were combined and dried with Na_2SO_4. The solution was filtered through a plug of silica gel and the solvents were removed in vacuo to yield a pale yellow liquid (40.6 g, 72%). The product was a mixture of stereoisomers and additionally contained ca. 35 mol % of (*E*)-2-nitrotetradec-2-ene. ^{1}H NMR (300 MHz, $CDCl_3$, relative intensities for the alkene are not to scale with those of the acetates) δ 7.10 (tq, ^3J = 8.2 Hz, ^4J = 1.0 Hz, 1H, C=C*H*), 5.22-5.31 (m, 1H, C*H*NO_2), 4.58-4.71 (m, 1H, C*H*OAc), 2.18 (~q, *J* = 7.7 Hz, 2H, C=CHCH_2), 2.12 (d, *J* = 1.0 Hz, 3H, C=C(NO_2)CH_3), 2.05, 2.04, 2.02 (3 × s, CH_3COO), 1.51, 1.49 (2 × d, *J* = 7.2, 3H, CH(NO_2)CH_3), 1.14-1.30 (m, alkyl CH_2) 0.84 (t, *J* = 6.7 Hz, 3H, CH_3). MS (CI+): 302.

1,2-Bis(decyloxy)-4-(2-nitroprop-1-enyl)benzene (3c). 3,4-Bis(decyloxy)benzaldehyde[4] (26.9 g, 64.3 mmol), ammonium acetate (4.96 g, 64.3 mmol), and nitroethane (130 mL, 2L/mol) were placed in a 500 mL round-bottomed flask equipped with a stirring bar and a reflux condenser. The mixture was heated at reflux with magnetic stirring for 17 hours, during which time the color changed from clear to brown. After that time, excess solvent was removed under reduced pressure; the residue was diluted with ethyl acetate (200 mL) and washed with water three times. The organic phase was dried with anhydrous sodium sulfate, and the solvent was removed on a rotary evaporator. The crude product was purified by flash column chromatography (silica, 8 cm × 25 cm; 10% ethyl acetate/hexanes, eluent) yielding **3c** as a yellow oil (19.5 g, 64%). TLC: R_f = 0.48 (10% ethyl acetate/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (t, ^4J = 0.9 Hz, 1H, CH_3C=C*H*Ar), 7.03 (dd, ^3J = 8.5 Hz, ^4J = 2.1 Hz, 1H, *ortho*), 6.95 (d, ^4J = 2.1 Hz, 1H, 2-Ar, *ortho*), 6.90 (d, ^3J = 8.5 Hz, 1H, *meta*), 4.02 (t, ^3J = 6.8 Hz, 2H, decyl α-CH_2), 3.99 (t, ^3J = 6.8 Hz, 2H, decyl α-CH_2), 2.46 (d, ^4J = 0.9 Hz, 1H, CH_3C=CHAr), 1.75–1.87 (m, 4H, decyl β-CH_2), 1.39–1.51 (m, 4H, decyl γ-CH_2), 1.15–1.39 (m, 24H, decyl CH_2), 0.86 (t, ^3J = 6.9 Hz, 6H, decyl CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.1, 149.0, 145.6, 134.0, 124.2, 117.2, 115.6, 113.0, 69.5, 69.0, 31.9, 29.0-29.6 (multiple peaks), 26.0, 22.7, 14.2, 14.1; HR-MS (CI+): *m*/*z* 476.3741 [M–H$^+$], calcd for $C_{29}H_{50}NO_4$: 476.3740.

1-Decyloxy-4-(2-nitroprop-1-enyl)benzene (3b) was obtained from 4-decyloxybenzaldehyde[4] (34 g, 130 mmol) using the same procedure as given for **3c**. Yield: 29.2 g (70%). R_f = 0.55 (10% ethyl acetate/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (t, ^4J = 0.9 Hz, 1H, C=C*H*), 7.93 (d, ^3J = 9.0 Hz, 2H, phenyl 3,5-H), 6.94 (d, ^3J = 9.0 Hz, 2H, phenyl 2,6-H), 3.98 (t, 2H, ^3J = 6.8 Hz, α-decyl), 2.46 (d, ^4J = 0.9 Hz, 3H, C=CC*H*$_3$), 1.78 (m, 2H, β-decyl), 1.44 (m, 2H, γ-decyl), 1.20-1.38 (m, 12H, decyl CH_2), 0.86 (t, ^3J = 6.8 Hz, 3H, decyl CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.72, 145.50, 133.74, 132.10, 124.44, 114.93, 68.22, 32.88, 29.54 (×2), 29.35, 29.31, 29.10, 25.99, 22.67, 14.15, 14.12; HR-MS (CI+): *m*/*z* 320.2212 [M+H$^+$], calcd for $C_{19}H_{30}NO_3$: 320.2226.

Ethyl 4-methyl-3-undecyl-1*H*-pyrrole-2-carboxylate (4a). Compound **2a** (5 g, 16.6 mmol) was dissolved in a mixture of THF (25 mL) and isopropyl alcohol (25 mL). Ethyl isocyanoacetate (1.88 g, 16.6 mmol) and K_2CO_3 (5 g, ca. 2 equiv.) were added and the reaction was stirred overnight. The reaction was judged complete by TLC analysis. The reaction mixture was poured into water, the organic phase was separated and the aqueous phase washed with ethyl acetate. The organic phases were combined, dried with Na_2SO_4, and the solvent w removed in vacuo. The crude product was purified by flash chromatography (silica gel, 10% ethyl acetate in hexanes) yielding white crystalline sold (3.75 g, 74%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.78 (b, 1H, NH), 6.62 (d, *J* = 2.7 Hz, 1H, α-H), 4.28 (q, *J* = 7.2 Hz, 2H, OC*H*$_2$CH$_3$), 2.69 (dd, 2H, undecyl α-CH_2), 2.00 (s, 3H, CH_3), 1.48 (m, 2H, undecyl β-CH_2), 1.33 (t, *J* = 7.2 Hz, 3H, OCH$_2$C*H*$_3$), 1.2–1.4 (m, 16H, undecyl CH_2's), 0.86 (t, *J* = 7.0 Hz, 3H, undecyl CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.68, 131.77, 120.25, 120.07, 118.88, 59.76, 31.91, 30.84, 29.81, 29.69 (×2), 29.65, 29.61, 29.35, 24.99, 22.69, 14.47, 14.11, 9.92; HR-MS (CI+): *m*/*z* 308.2591 [M–H$^+$], calcd for $C_{19}H_{34}NO_2$: 308.2590.

Ethyl 3-(3,4-bis(decyloxy)phenyl)-4-methylpyrrole-2-carboxylate (4c). A 250 mL round-bottomed flask equipped with a stirring bar was charged with a mixture of tetrahydrofuran (40 mL) and isopropyl alcohol (40 mL). Compound **3b** (10 g, 21 mmol) was then added, followed by ethyl isocyanoacetate (2.30 mL, 21 mmol). With stirring, DBU (3.13 mL, 21 mmol) was added dropwise, and the reaction mixture was left to stir for 21 hours. The reaction mixture was diluted with water (200 mL), the organic layer was separated, and the aqueous layer was extracted with ethyl acetate (2 × 150 mL). The combined organic fractions were stripped of solvent using a rotary evaporator. The resulting residue was purified by flash column chromatography (silica, 8 cm × 15 cm; 20% ethyl acetate/hexanes, eluent). Fractions containing the product were combined and the solvent was removed under vacuum. Pure **4c** was obtained as a yellowish solid (10.33 g, 91%). TLC: R_f = 0.17 (10% ethyl acetate/hexanes), 0.36 (20% ethyl acetate/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.93 (bs, 1H, N*H*), 6.80–6.90 (m, 3H, *ortho* + *meta*),

6.74 (dd, ^4J = 3.0 Hz, ^4J = 0.9 Hz, 1H, 2-H), 4.15 (q, ^3J = 6.8 Hz, 2H, OC*H*$_2$CH$_3$), 4.01 (t, ^3J = 6.8 Hz, 2H, decyl α-CH$_2$), 3.97 (t, ^3J = 6.8 Hz, 2H, decyl α-CH$_2$), 1.98 (d, ^4J = 0.9 Hz, 3H, pyrrole CH$_3$), 1.74–1.87 (m, 4H, decyl β-CH$_2$), 1.36–1.51 (m, 4H, decyl γ-CH$_2$), 1.17–1.36 (m, 24H, decyl CH$_2$), 1.14 (t, ^3J = 7.3 Hz, 3H, OCH$_2$C*H*$_3$), 0.87 (t, ^3J = 6.8 Hz, 3H, decyl CH$_3$), 0.86 (t, ^3J = 6.8 Hz, 3H, decyl CH$_3$); ^{13}C NMR (75 MHz, CDCl$_3$) δ 161.2, 148.1, 148.0, 130.9, 127.3, 122.9, 120.5, 120.2, 118.8, 116.4, 113.0, 69.2 (×2), 59.9, 31.9 (×2), 29.7 (×2), 29.6 (×2), 29.5 (×2), 29.4, (×2), 29.3 (×2), 26.1 (×2), 22.7 (×2), 14.2, 14. (×2), 10.7; HR-MS (CI+): *m*/*z* 541.4130 [M$^+$], calcd for C$_{34}$H$_{55}$NO$_4$: 541.4131.

Ethyl 3-(4-decyloxyphenyl)-4-methylpyrrole-2-carboxylate (4b) was obtained from **3b** (29.2 g, 91.5 mmol) using the same procedure as given for **4c**. White solid. Yield: 16.1 g (46%). R_f = 0.18 (10% ethyl acetate/hexanes); ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.91 (bs, 1H, N*H*), 7.24 (d, ^3J = 9.0 Hz, 2H, phenyl 3,5-H), 6.89 (d, ^3J = 9.0 Hz, 2H, phenyl 2,6-H), 6.74 (dq, ^3J = 3.0 Hz, ^4J = 0.9 Hz, 1H pyrrole α-H), 4.15 (q, ^3J = 7.3 Hz, 2H, OC*H*$_2$CH$_3$), 3.97 (t, ^3J = 6.8 Hz, 2H, α-decyl), 1.98 (d, ^4J = 0.9 Hz, 3H, pyrrole CH$_3$), 1.78 (m, 2H, β-decyl), 1.45 (m, 2H, γ-decyl), 1.20-1.38 (m, 12H, decyl CH$_2$), 1.15 (t, ^3J = 7.3 Hz, 3H, OCH$_2$C*H*$_3$), 0.87 (t, ^3J = 6.8 Hz, 3H, decyl CH$_3$); ^{13}C NMR (75 MHz, CDCl$_3$) δ 161.12, 158.00, 131.34, 130.88, 126.59, 120.43, 120.26, 118.77, 113.50, 67.93, 59.90, 29.60, 29.57, 29.42, 29.35, 29.32 (×2), 26.09, 22.68, 14.20, 14.12, 10.61; HR-MS (CI+): *m*/*z* 385.2628 [M$^+$], calcd for C$_{24}$H$_{35}$NO$_3$: 285.2617.

Ethyl 5-iodo-4-methyl-3-undecyl-1*H*-pyrrole-2-carboxylate (5a). Iodine (8.2 g, 32 mmol), sodium iodide (10.2 g, 68 mmol), and NaHCO$_3$ (2.7 g, 32 mmol) were dissolved in water (500 mL) with gentle heating. **2** (7.6 g, 25 mmol) in 1,2-dichloroethane (500 mL) was added, and the reaction mixture was refluxed overnight, after which time all starting material was consumed. Aqueous Na$_2$S$_2$O$_3$ was added to the cooling mixture. The layers were then separated and the organic layer washed with dichloromethane. The organic fractions were combined, washed with dilute aqueous Na$_2$S$_2$O$_3$ and with brine. The extracts were dried over Na$_2$SO$_4$ and the solvents were removed under reduced pressure to yield a brownish crystalline solid (7.82 g, 76%). ^{1}H NMR (300 MHz, CDCl$_3$) δ 9.42 (b, 1H, NH), 4.36 (q, J = 7.2 Hz, 2H, OC*H*$_2$CH$_3$), 2.75 (dd, 2H, undecyl α-CH$_2$), 1.99 (s, 3H, CH$_3$), 1.50 (m, 2H, undecyl β-CH$_2$), 1.38 (t, J = 7.2 Hz, 3H, OCH$_2$C*H*$_3$), 1.2–1.4 (m, 16H, undecyl CH$_2$'s), 0.90 (t, J = 7.0 Hz, 3H, undecyl CH$_3$); ^{13}C NMR (75 MHz, CDCl$_3$) 160.83, 132.04, 125.62, 123.25, 73.89, 60.17, 43.36, 31.88, 30.67, 29.64, 29.62, 29.60, 29.52, 29.31, 25.72, 22.65, 14.41, 14.08, 11.81; MS (CI+): 434.

Ethyl 3-(4-decyloxyphenyl)-5-iodo-4-methyl-1H-pyrrole-2-carboxylate (5b) was obtained from **4b** (11 g, 28.5 mmol) using the same procedure as given for **5a**. Pinkish solid. Yield: 11.9 g (81%). R_f = 0.24 (10% ethyl acetate/hexanes); ^{1}H NMR (300 MHz, CDCl$_3$) δ 9.15 (bs, 1H, N*H*), 7.19 (d, ^3J = 9.0 Hz, 2H, phenyl 3,5-H), 6.89 (d, ^3J = 9.0 Hz, 2H, phenyl 2,6-H), 4.16 (q, ^3J = 7.3 Hz, 2H, OC*H*$_2$CH$_3$), 3.96 (t, ^3J = 6.8 Hz, 2H, α-decyl), 1.92 (s, 3H, pyrrole CH$_3$), 1.78 (m, 2H, β-decyl), 1.45 (m, 2H, γ-decyl), 1.38-1.20

(m, 12H, decyl CH_2), 1.15 (t, ^3J = 7.3 Hz, 3H, OCH_2CH_3), 0.87 (t, ^3J = 6.8 Hz, 3H, decyl CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.15, 158.31, 131.22, 126.17, 126.06, 123.13, 113.57, 113.50, 73.76, 67.96, 60.24, 31.90, 29.60, 29.57, 29.42, 29.32 (×2), 26.09, 22.68, 14.18, 14.13, 12.65; HR-MS (CI+): *m*/*z* 512.1650 [M+H$^+$], calcd for $C_{24}H_{35}NO_3I$: 512.1662.

Ethyl 3-(3,4-bis(decyloxy)phenyl)-5-iodo-4-methyl-1H-pyrrole-2-carboxylate (5c) was obtained from **4c** (8.13 g, 15 mmol) using the same procedure as given for **5a**. The product was purified by flash column chromatography (silica, 8 cm × 25 cm; 15% ethyl acetate/hexanes, eluent). Fractions containing the product were combined and the solvent was removed under vacuum. Product **5c** was obtained as a pinkish solid (5.85 g, 58%). TLC: R_f = 0.56 (20% ethyl acetate/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.23 (bs, 1H, N*H*), 6.75–6.90 (m, 3H, *ortho* + *meta*), 4.16 (q, ^3J = 6.8 Hz, 2H, OCH_2CH_3), 4.00 (t, ^3J = 6.8 Hz, 2H, decyl α-CH_2), 3.95 (t, ^3J = 6.8 Hz, 2H, decyl α-CH_2), 1.92 (s, 3H, pyrrole CH_3), 1.73–1.87 (m, 4H, decyl β-CH_2), 1.37–1.52 (m, 4H, decyl γ-CH_2), 1.17–1.37 (m, 24H, decyl CH_2), 1.13 (t, ^3J = 7.1 Hz, 3H, OCH_2CH_3), 0.863 (t, ^3J = 6.8 Hz, 3H, decyl CH_3), 0.858 (t, ^3J = 6.8 Hz, 3H, decyl CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.2, 148.3, 148.1, 131.3, 126.7, 126.2, 123.2, 122.7, 116.2, 112.9, 73.8, 69.25, 69.21, 60.2, 31.9 (×2), 29.63 (×2), 29.58 (×2), 29.4 (×2), 29.3 (×4), 26.0 (×2), 22.7 (×2), 14.2, 14.1 (×2), 12.7; HR-MS (CI+): *m*/*z* 667.3093 [M$^+$], calcd for $C_{34}H_{54}NO_4I$: 667.3098.

5,5'-Diethoxycarbonyl-3,3'-dimethyl-4,4'-diundecyl-2,2'-bipyrrole (6a). 5a (7.27 g, 16.8 mmol) was dissolved in dichloromethane (50 mL) and di-*t*-butyl dicarbonate (4.1 g, 1.1 equiv.) was added. DMAP (60 mg) was added and the mixture was stirred until no starting material could be detected by TLC analysis (1–2 h). Silica gel (5 g) was added, the mixture was stirred for 5 minutes, filtered, and the silica was washed with dichloromethane. The filtrates were combined and the solvent was removed in vacuo. The residue, containing the Boc-protected **5a** was, was dissolved in toluene (4 mL) and copper powder (7 g) was added. The mixture was refluxed for 16 hours (magnetic stirring, argon atmosphere). After this time, all starting material was consumed. The mixture was filtered through Celite, the reaction mixture and the Celite plug were rinsed with toluene, and the filtrates were combined. The solvent was removed in vacuo. The crude product was purified by flash column chromatography (silica gel, 10% ethyl acetate in hexanes) to yield pure **6a** as a greyish solid (3.82 g, 74%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.92 (bs, 2H, NH), 4.26 (q, 4H, OCH_2CH_3), 2.72 (dd, 4H, undecyl α-CH_2), 2.02 (s, 6H, CH_3), 1.50 (m, 4H, undecyl β-CH_2), 1.32 (t, *J* = 7.2 Hz, 6H, OCH_2CH_3), 1.2–1.4 (m, 32H, undecyl CH_2's), 0.86 (t, *J* = 6.3 Hz, 6H, undecyl CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.56, 132.66, 124.73, 119.11, 118.90, 59.98, 31.91, 30.79, 29.84, 29.69 (×2), 29.65, 29.60, 29.35, 25.23, 22.68, 14.44, 14.10, 9.88; MS (CI+): *m*/*z* 613.9 [M+H$^+$].

Diethyl 4,4'-bis(4-decyloxyphenyl)-3,3'-dimethyl-2,2'-bipyrrole-5,5'-dicarboxylate (6b) was obtained from **5b** (11.9 g, 23.3 mmol) using the same procedure as given for **6a**. Crystallized from CH_2Cl_2/MeOH. Yellowish solid. Yield: 7.77 g (87%). R_f = 0.32 (20% ethyl acetate/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.03 (bs, 2H, N*H*), 7.26 (d, ^3J = 9.0 Hz, 4H, phenyl 3,5-H), 6.92 (d, ^3J = 9.0 Hz, 4H, phenyl 2,6-H), 4.17 (q, ^3J = 7.3 Hz, 4H, OC*H*$_2$CH$_3$), 3.98 (t, ^3J = 6.8 Hz, 4H, α-decyl), 2.05 (s, 6H, pyrrole CH_3), 1.79 (m, 4H, β-decyl), 1.46 (m, 4H, γ-decyl), 1.38-1.20 (m, 24H, decyl CH_2), 1.16 (t, ^3J = 7.3 Hz, 6H, OCH$_2$C*H*$_3$), 0.87 (t, ^3J = 6.8 Hz, 6H, decyl CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.00, 158.23, 131.96, 131.39, 126.20, 124.49, 119.55, 118.94, 113.61, 67.96, 60.16, 31.89, 29.59, 29.56, 29.43, 29.35, 29.32, 26.10, 22.68, 14.20, 14.11, 10.82; HR-MS (FAB+): *m*/*z* 768.5074 [M^+], calcd for $C_{48}H_{68}N_2O_6$: 768.5077.

Diethyl 4,4'-bis(3,4-bis(decyloxy)phenyl)-3,3'-dimethyl-2,2'-bipyrrole-5,5'-dicarboxylate (6c) was obtained from **5c** (5.85 g, 8.76 mmol) using the same procedure as given for **6a**. Purified using flash column chromatography (silica, 4.5 cm × 30 cm; 15% ethyl acetate/hexanes, eluent). The fractions containing the product were combined and the solvent was removed under reduced pressure. The product (compound **6c**) was obtained as a yellow amorphous solid (3.3 g, 70%). TLC: R_f = 0.44 (20% ethyl acetate/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.98 (bs, 1H, N*H*), 6.83–6.93 (m, 3H, *ortho* + *meta*), 4.17 (q, ^3J = 6.8 Hz, 2H, OC*H*$_2$CH$_3$), 4.02 (t, ^3J = 6.8 Hz, 2H, decyl α-CH_2), 3.98 (t, ^3J = 6.8 Hz, 2H, decyl α-CH_2), 2.05 (s, 3H, pyrrole CH_3), 1.73–1.88 (m, 4H, decyl β-CH_2), 1.39–1.51 (m, 4H, decyl γ-CH_2), 1.19–1.39 (m, 24H, decyl CH_2), 1.15 (t, ^3J = 7.1 Hz, 3H, OCH$_2$C*H*$_3$), 0.86 (t, ^3J = 6.8 Hz, 3H, decyl CH_3), 0.85 (t, ^3J = 6.8 Hz, 3H, decyl CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.2, 148.29, 148.26, 132.0, 127.0, 124.6, 123.0, 119.6, 119.0, 116.5, 113.1, 69.4, 69.3, 60.1, 31.9 (×2), 29.64 (×2), 29.58 (×2), 29.5 (×2), 29.4 (×2), 29.3 (×2), 26.1 (×2), 22.7 (×2), 14.2, 14.1 (×2), 10.9. HR-MS (CI+): *m*/*z* 1081.8179 [M–H^+], calcd for $C_{68}H_{109}N_2O_8$: 1081.8184.

General procedure for saponification and decarboxylation of bipyrroles 6a-c. In a 50 mL round bottomed flask equipped with a reflux condenser and magnetic stir bar were placed **6a-c** (2.0 mmol), KOH (0.45 g, 8.0 mmol), and ethylene glycol (20 mL) under the atmosphere of argon. The vessel was immersed in an oil bath preheated to 190 °C and heated for 5 hours with vigorous stirring. After this time, no starting material could be detected by TLC analysis. The reaction was allowed to cool down without stirring. The product separated as the top layer and solidified upon cooling. The glycol solution was removed; the wax-like solid was rinsed with water several times and left to dry under high vacuum. The product was carried on to the next step without further purification.

3,3'-Dimethyl-4,4'-diundecyl-2,2'-bipyrrole (7a). From **6a** (1.22 g, 2.0 mmol). Yield: 0.83 g (88%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (bs, 2H, NH), 6.53 (d, *J* = 2.4 Hz, 2H, pyrrole α-H), 2.41 (dd, 4H, undecyl α-CH_2), 2.01 (s, 6H, CH_3), 1.57 (m, 4H, undecyl β-CH_2), 1.2–1.4 (m, 32H, undecyl CH_2's), 0.87

(t, J = 6.3 Hz, 6H, undecyl CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) 124.48, 121.82, 115.49, 31.93, 30.20, 29.79, 29.71, 29.70, 29.69, 29.67, 29.60, 29.36, 25.68, 22.69, 14.12, 9.88; MS (CI+): 469.

4,4'-Bis(4-decyloxyphenyl)-3,3'-dimethyl-2,2'-bipyrrole (7b). From **6b** (3.59 g, 4.67 mmol). Greenish solid. Yield: 2.66 g (91%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (bd, ^3J = 2.6 Hz, 2H, N*H*), 7.36 (d, ^3J = 9.0 Hz, 4H, phenyl 3,5-H), 6.92 (d, ^3J = 9.0 Hz, 4H, phenyl 2,6-H), 6.86 (d, ^3J = 2.6 Hz, 2H, pyrrole α-H), 3.97 (t, ^3J = 6.8 Hz, 4H, α-decyl), 2.19 (s, 6H, pyrrole CH_3), 1.78 (m, 4H, β-decyl), 1.45 (m, 4H, γ-decyl), 1.38-1.20 (m, 24H, decyl CH_2), 0.87 (t, ^3J = 6.8 Hz, 6H, decyl CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.38, 128.60, 128.61, 125.39, 122.38, 115.23, 115.13, 114.44, 68.03, 31.89, 29.59, 29.56, 29.43, 29.36, 29.32, 26.08, 22.68, 14.11, 11.20; HR-MS (CI+): *m*/*z* 624.4652 [M^+], calcd for 624.4655: $C_{42}H_{60}N_2O_2$.

4,4'-Bis(3,4-bis(decyloxy)phenyl)-3,3'-dimethyl-2,2'-bipyrrole (7c). From **6c** (1.08 g, 1.0 mmol). The product proved unstable and was thus immediately carried on to the next step. TLC: R_f = 0.46 (20% ethyl acetate/hexanes).

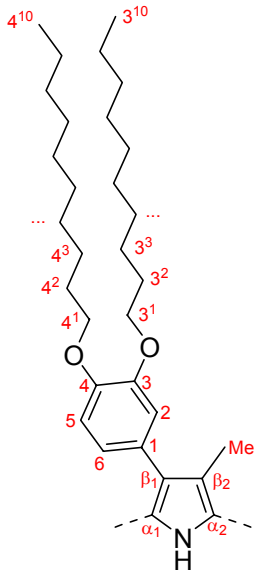
General procedure for the synthesis of cyclo[8]pyrroles 1a-c. A three-necked 1-L round-bottom flask was charged with a stir bar, dichloromethane (500 mL), and a solution of $FeCl_3 \cdot 6\ H_2O$ (2.7 g, 10 mmol) in 1 M sulfuric acid (100 mL). The resulting biphasic mixture was stirred at 300 rpm, while a solution of the bipyrrole **7a-c** (ca. 1mmol) in dichloromethane (50 mL) was added slowly using a syringe pump (Sage, model M365) over a period of at least 9 h, with the needle submerged into the organic phase. Throughout the addition, the flask and syringe were carefully protected from light. After completion of the addition, the reaction mixture was stirred for 5 h. Subsequently, the phases were separated and the organic phase was dried over anhydrous sodium sulfate. After filtration through a fluted paper filter to remove any residual solid matter, the solvent was removed in vacuo. The crude product was purified twice by flash column chromatography (silica, 4.5 cm × 30 cm for both columns, using 1:1 diethyl ether-hexanes as the eluent for the first column and then 1:2 diethyl ether-hexanes for the second). The desired product, **6**, eluted as the first major fraction in the form of a deep brown band, followed by sizable amounts of byproducts. The solvent was removed in vacuo, and the residue triturated with hot methanol.

2,7,10,15,18,23,26,31-octamethyl-3,6,11,14,19,22,27,30-octaundecylcyclo[8]pyrrole, sulfate salt (1a). From **7a** (0.43 g, 0.92 mmol); addition time 9 h. Crystallization was induced by sonicating the product under high vacuum. Yield: 230 mg (51%). UV-vis (CH_2Cl_2, 298 K) λ_{max} [nm] (log ε, ε in $M^{-1}cm^{-1}$): 432 (4.87), 1128 (5.09). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.08 (b, 16H, undecyl α-CH_2), 3.68 (b, 24H, CH_3), 2.24 (m, 16H, undecyl β-CH_2), 1.64 (m, 16H, undecyl γ-CH_2), 1.47 (m, 16H, undecyl δ-CH_2), 1.35–1.20 (m, 96H, undecyl CH_2), 0.85 (m, 24H, undecyl CH_3); ^{13}C NMR (126 MHz, $CDCl_3$, signals of α and β pyrrole carbons were dynamically broadened and could not be observed, partial assignment based on a

^{1}H-^{13}C HSQC spectrum) δ 31.92, 31.7 (b, undecyl β-CH_2), 30.65 (undecyl γ-CH_2), 29.80, 29.77 (× 2), 29.70, 29.37, 29.2 (b, undecyl α-CH_2), 22.68, 15.85 (b, CH_3) 14.10 (undecyl CH_3); HR-MS (ESI+): *m*/*z* 1295.9214 [M–H$^+$], calcd for $C_{28}H_{119}N_4O_4$: 1295.9231. Elemental analysis for $C_{128}H_{216}N_8O_4S$: calcd. C 78.31, H 11.09, N 5.71; found C 78.63, H 11.10, N 5.70.

2,7,10,15,18,23,26,31-Octakis(4-decyloxyphenyl)-3,6,11,14,19,22,27,30-octamethylcyclo[8]pyrrole, sulfate salt (1c). From **7b** (625 mg, 1 mmol); addition time 35 h. Yield: 461 mg (71%). UV-vis (CH_2Cl_2, 298 K) λ_{max} [nm] (log ε, ε in $M^{-1}cm^{-1}$): 466 (5.02), 1122 (5.34). ^{1}H NMR (500 MHz, 298 K, $CDCl_3$, labeling follows that given in Scheme S2, partial broadening is due to conformational exchange) δ 7.42 (b, 16H, 2,6-H), 6.97 (d, *J* = 8.7 Hz, 16H, 3,5-H), 4.19 (t, *J* = 6.5 Hz, 16H, 4^1-H), 3.76 (s, 24-H, Me), 2.00 (m, 16H, 4^2-H), 1.66 (m, 16H, 4^3-H), 1.53 (m, 16H, 4^4-H), 1.48–1.24 (m, 80H, 4^5–4^9-H), 0.92 (t, *J* = 6.5 Hz, 24H, 4^{10}-H). ^{13}C NMR (126 MHz, 298 K, $CDCl_3$, partial assignments obtained from HSQC and HMBC spectra, labeling follows that given in Scheme S2) δ 157.89 (4), 133.82 (2,6), 131.36 (1), 129.91, 125.85, 125.22, 124.54, 114.25 (3,5), 68.21 (4^1), 31.99, 29.81, 29.74, 29.63 (×2), 29.45, 26.38, 22.76, 16.79 (Me), 14.16 (4^{10}). Elemental analysis for $C_{168}H_{232}N_8O_{12}S$: calcd. C 77.97, H 9.04, N 4.33; found C 77.94, H 9.07, N 4.35. HRMS (ESI+): *m*/*z* 2586.7581 [M–H$^+$], calcd for $C_{168}H_{233}N_8O_{12}S^+$: 2586.7589.

2,7,10,15,18,23,26,31-Octakis(3,4-bis(decyloxy)phenyl)-3,6,11,14,19,22,27,30-octamethylcyclo-[8]pyrrole, sulfate salt (1c). From **7c** (0.94 g, 1 mmol); addition time 38 h. Yield: 313 mg (33%). UV-vis (CH_2Cl_2, 298 K) λ_{max} [nm] (log ε, ε in $M^{-1}cm^{-1}$): 468 (4.96), 1138 (5.28). ^{1}H NMR (500 MHz, 333 K, $CDCl_3$, labeling follows that given in Scheme S2, partial broadening is due to conformational exchange) δ 7.11 (b, 8H, 6-H), 7.02 (b, 8H, 2-H), 7.00 (d, *J* = 8.5 Hz, 8H, 5-H), 4.24 (t, *J* = 6.5 Hz, 16H, 4^1-H), 3.94 (b, 16H, 3^1-H), 3.74 (s, 24H, Me), 2.02 (m, 16H, 4^2-H), 1.83 (b, 16H, 3^2-H), 1.68 (m, 16H, 4^3-H), 1.53 (m, 16H, 3^3-H), 1.55-1.10 (m, 96H, 4^4–4^9,3^4–3^9-H), 0.95 (t, *J* = 6.5 Hz, 24H, 4^{10}-H), 0.83 (t, *J* = 6.5 Hz, 24H, 3^{10}-H), –0.38 (s, 8H, NH). ^{13}C NMR (126 MHz, 333 K, $CDCl_3$, shift values and assignments obtained from high resolution HSQC and HMBC spectra, labeling follows that given in Scheme S2) δ 149.2 (3), 148.4 (4), 131.9 (β_1), 130.6 (1), 126.4 (α_2), 126.0 (α_1), 125.8 (6), 124.3 (β_2), 119.1 (2), 114.7 (5), 70.0 (4^1), 69.4 (3^1), 32.1 (4^8), 32.0 (3^8), 30.0 (4^2), 29.8 (3^2), 30.0–29.4 (multiple peaks: 4^4–4^7, 3^4–3^7), 26.5 (4^3), 26.4 (3^3), 22.7 (4^9), 22.6 (3^9), 16.7 (Me), 14.0 (4^{10}), 13.9 (3^{10}). Elemental analysis for $C_{248}H_{392}N_8O_{20}S$: calcd. C 77.61, H 10.30, N 2.92; found C 77.74, H 10.23, N 2.93. MS (ESI+): *m*/*z* 3840 [M–H$^+$], calcd for $C_{248}H_{393}N_8O_{20}S^+$: 3838.9; 1921 [M–2H^{2+}], calcd for $C_{248}H_{394}N_8O_{20}S^{2+}$: 1920.0.



Scheme S2. Labeling scheme for the symmetry-independent part of **1c**. For **1b** the 3-decyloxy substituent should be ignored.

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