

Supporting information

Self-assembly of corrole trimers in solution and at the solid-liquid interface

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General experimental part.

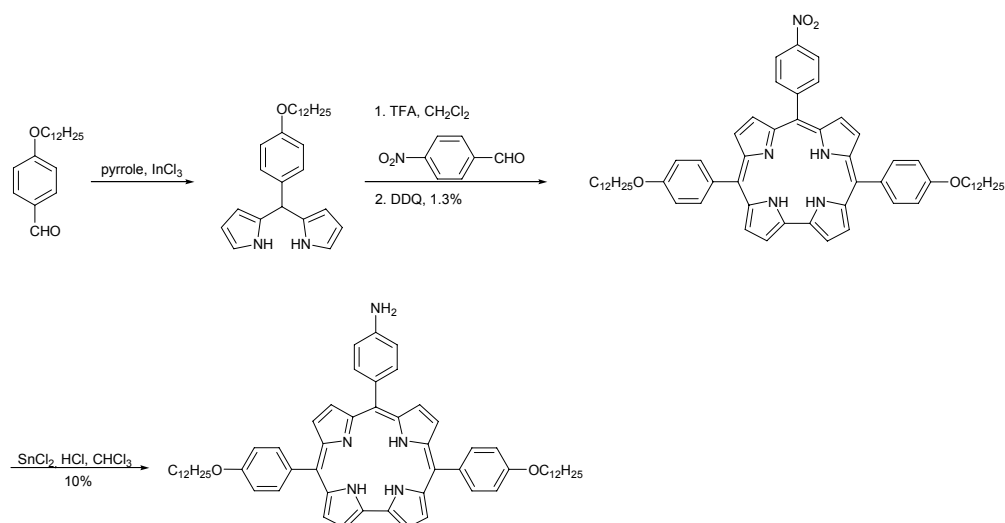
All chemicals were used as received unless otherwise noted. Reagent grade solvents (CH₂Cl₂, hexanes, cyclohexane) were distilled prior to use. All reported ¹H NMR and ¹³C NMR spectra were recorded on Bruker AM 500 MHz or Varian 400 MHz spectrometers. Chemical shifts (δ ppm) were determined with TMS as the internal reference; *J* values are given in Hz. UV-Vis spectra were recorded on a Varian Cary 50 conc spectrometer operating at room temperature. Chromatography was performed on silica (Kieselgel 60, 200-400 mesh), or dry column vacuum chromatography (DCVC) was performed on preparative thin layer chromatography silica (Merck 107747). Mass spectra were obtained *via* EI, electrospray or FD MS. Elemental analysis was measured with a Carbo Erba Ea 1108 instrument.

Syntheses

5-(4-Dodecyloxyphenyl)dipyrromethane. A mixture of pyrrole (173 mL, 2.5 mol) and 4-dodecyloxybenzaldehyde (7.26 g, 25 mmol) was degassed with a stream of argon for 10 min. InCl₃ (555 mg, 2.5 mmol) was added, and the mixture was stirred under argon at room temperature for 1.5 h. The reaction was quenched by the addition of powdered NaOH (3 g, 75 mmol). The mixture was stirred for 1 h and then filtered through pad of celite. The excess pyrrole was removed under reduced pressure and the resulting oil was used in the crude form in the next step. HRMS (EI): *m/z* calcd. for C₂₇H₃₈N₂O 406.2984; found 406.2998.

5,15-Bis(4-dodecyloxyphenyl)-10-(4-nitrophenyl)corrole. A sample of 5-(4-Dodecyloxyphenyl)dipyrrromethane (325 mg, 0.8 mmol) and 4-nitrobenzaldehyde (60 mg, 0.4 mmol) were dissolved in 24 mL of pre-prepared solution of TFA (7.5 μ L, 98 μ mol) in CH_2Cl_2 (100 mL). After 1.5 h at room temperature *p*-chloranil (295 mg, 1.2 mmol) was added and the reaction mixture was stirred at room temperature for further 1 h. The reaction mixture was concentrated. Chromatography [silica, CH_2Cl_2 /heksan (1:1)] afforded a dark solid which was crystallized from CHCl_3 /methanol to give pure corrole (5 mg, 1.3 %). R_f = 0.53 (silica; CH_2Cl_2 /hexane, 3:2); ^1H NMR (200 MHz, CDCl_3): δ 0.90 (t, 6H, J = 6.5 Hz, CH_3), 1.37 (m, 28H, CH_2), 1.47 (m, 4H, CH_2), 1.63 (m, 4H, CH_2), 1.97 (br s, 4H, CH_2), 4.23 (br s, 4H, OCH_2), 7.31 (br s, 4H, Ar), 8.10 (br s, 6H, Ar), 8.27 (br s, 4H, Ar), 8.52 (br s, 4H, Ar), 8.74 (br s, 2H, Ar); LRMS (FD): m/z calcd. for $\text{C}_{61}\text{H}_{73}\text{N}_5\text{O}_4$ 939.6; found 939.6. Anal. calc. for $\text{C}_{61}\text{H}_{73}\text{N}_5\text{O}_4$: C, 77.92; H, 7.83; N, 7.45. Found: C, 77.98; H, 7.55; N, 7.46%. UV-Vis (CH_2Cl_2): λ_{max} /nm 421, 584, 614, 653.

5,15-Bis(4-dodecyloxyphenyl)-10-(4-aminophenyl)corrole. To the solution of 5,15-bis(4-dodecyloxyphenyl)-10-(4-nitrophenyl)corrole (0.049 mmol, 46.5 mg) in CHCl_3 (6.5 mL) the solution of SnCl_2 (1.2 mmol, 235 mg in HCl 35 % (3.8 mL)) was added. The reaction mixture was stirred at RT for 2 hours. Subsequently NH_3 aq. (3.5 mL) was added and the resulting emulsion was diluted with water and extracted with CH_2Cl_2 . Organic phase was dried and evaporated to obtain 4.4 mg (10 %) aminophenylcorrole, which was not stable during chromatography. R_f = 0,36 (SiO_2 , CH_2Cl_2 /hexanes 3:2); LRMS (FD): m/z calcd. for $\text{C}_{61}\text{H}_{75}\text{N}_5\text{O}_2$; 909.59 found 909.7.



Scheme SI-1. Preparation of highly unstable 5,15-bis(4-dodecyloxyphenyl)-10-(4-aminophenyl)corrole.

1-Dodecyloxy-2,3,5,6-tetrafluorobenzene. 18-Crown-6 (730 mg, 2.77 mmol) was added to the solution of 2,3,5,6-tetrafluorophenol (**2**) (5 g, 30 mmol), K_2CO_3 (6.22 g, 45 mmol) and 1-bromododecan (8.67 mL, 3.6 mmol) in acetone (50 mL). The mixture was stirred at reflux for 48 h. The reaction was cooled to room temperature, filtered and concentrated in vacuum. Purification by column chromatography (silica, CH_2Cl_2 /heksan 1:3) afforded 1-dodecyloxy-2,3,5,6-tetrafluorobenzene (9.35 g, 93 %). R_f = 0.53 (silica; CH_2Cl_2 /hexane, 3:2); 1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, 3H, J = 6.8 Hz, CH_3), 1.28 (m, 16H, CH_2), 1.45 (m, 2H, CH_2), 1.77 (m, 2H, CH_2), 4.21 (t, 2H, J = 6.6 Hz, OCH_2), 6.75 (m, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 22.6, 25.9, 29.2, 29.3, 29.4, 29.5, 29.5, 29.6, 29.9, 31.9, 75.3, 99.2, 138.5, 142.3, 141.1, 146.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ -140.8, -157.6; HRMS (EI): m/z calcd. for $C_{18}H_{26}F_4O$ 334.1920; found 334.1925. Anal. calc. for $C_{18}H_{26}F_4O$: C, 64.65; H, 7.84. Found: C, 64.57; H, 7.89%.

4-Dodecyloxy-2,3,5,6-tetrafluorobenzaldehyde (3). A solution of 1-dodecyloxy-2,3,5,6-tetrafluorobenzene (9.3 g, 28 mmol) in dry THF (59 mL) was placed in a three-necked flask equipped with magnetic stirrer. The flask was cooled to $-78^\circ C$ with a dry ice-acetone bath and 130 mL of a 1.0 M solution of *n*-butyl lithium were slowly added via a syringe under argon. The mixture was stirred for 1 h at $-78^\circ C$ then methyl formate

(3.50 mL, 57 mmol) was added at this temperature. After addition of methyl formate the cold bath was removed and the mixture was slowly warmed to room temperature. The reaction mixture was poured into saturated aqueous NaHCO₃ solution. The organic layer was separated, dried (MgSO₄) and concentrated. Chromatography [silica, CH₂Cl₂/heksan (2:3)] afforded crystals (9.5 g, 94 %). R_f = 0.53 (silica; CH₂Cl₂/hexane, 3:2); ¹H NMR (400 MHz, CDCl₃): δ 0.88 (t, 3H, *J* = 6.8 Hz, CH₃), 1.26 (m, 16H, CH₂), 1.46 (m, 2H, CH₂), 1.81 (m, 2H, CH₂), 4.41 (tt, 2H, *J*₁ = 1.5 Hz, *J*₂ = 7.0 Hz, OCH₂), 10.22 (br s, 1H, CHO); ¹³C NMR (100 MHz, CDCl₃): δ 14.1, 22.7, 25.4, 29.1, 29.3, 29.5, 29.5, 29.6, 29.9, 30.9, 31.9, 75.4, 108.7, 140.3, 143.1, 147.8, 146.4, 182.2, 206.9; HRMS (ESI): calcd. for C₁₉H₂₆F₄O₂Na 385.1761; found 385.1742. Anal. calc. for C₁₉H₂₆F₄O₂: C, 62.97; H, 7.23. Found: C, 62.85; H, 7.13%.

5-(4-Dodecyloxy-2,3,5,6-tetrafluorophenyl)dipyrromethane (4). A mixture of pyrrole (152 mL, 2.2 mol) and aldehyde **3** (8.0 g, 22 mmol) was degassed with a stream of argon for 10 min. InCl₃ (488 mg, 2.2 mmol) was added, and the mixture was stirred under argon at room temperature for 1.5 h. The reaction was quenched by the addition of powdered NaOH (2.6 g, 65 mmol). The mixture was stirred for 1 h and then filtered through pad of celite. The excess pyrrole was removed under reduced pressure and the resulting oil (10.1 g, 96 %) was used in the crude form in the next step. R_f = 0.53 (silica; CH₂Cl₂/hexane, 3:2); HRMS (EI): *m/z* calcd. for C₂₇H₃₄F₄N₂O 478.2607; found 478,2625.

5,15-Bis-(4-dodecyloxy-2,3,5,6-tetrafluorophenyl)-10-(4-phthalimidophenyl)corrole. A sample of dipyrromethane **4** (1.92 g, 4.0 mmol) and 4-phthalimidobenzaldehyde (**5**) (502 mg, 2.0 mmol) were dissolved in 30 mL of pre-prepared solution of TFA (100 μL, 1.3 mmol) in CH₂Cl₂ (100 mL). After 20 min at room temperature, the reaction mixture was diluted to 40 mL with CH₂Cl₂ and added to vigorously stirred CH₂Cl₂ (50 mL) simultaneously with the solution of DDQ (1.18 g, 5.2 mmol) in toluene (40 mL) over 20 min, and the reaction was stirred at room temperature for further 20 min. The reaction mixture was evaporated with silica and put on the top of chromatography column [silica, CH₂Cl₂/heksane (3:2)]. All fractions containing contaminated corrole were combined and evaporated. Subsequent chromatography [silica, CH₂Cl₂/heksan (3:2)] afforded pure

corrole (135 mg, 5.7 %). $R_f = 0.56$ (silica; $\text{CH}_2\text{Cl}_2/\text{hexane}$, 3:2); ^1H NMR (500 MHz, CDCl_3): δ 0.89 (t, 6H, $J = 6.9$ Hz, CH_3), 1.31 (m, 28H, CH_2), 1.48 (m, 4H, CH_2), 1.64 (tt, 4H, $J_1 = 7.6$ Hz, $J_2 = 15.4$ Hz, CH_2), 1.99 (tt, 4H, $J_1 = 7.1$ Hz, $J_2 = 15.1$ Hz, CH_2), 4.54 (t, 4H, $J = 6.54$ Hz, OCH_2), 7.84 (dd, 2H, $J_1 = 3.02$ Hz, $J_2 = 5.35$ Hz, Ar), 7.87, 8.33 (AA'BB', 4H, $J = 8.3$ Hz), 8.05 (dd, $J_1 = 3.01$ Hz, $J_2 = 5.36$ Hz, 2H, Ar), 8.59 (br s, 2H, β -H), 8.77 (br s, 4H, β -H), 9.08 (d, 2H, $J = 4.2$ Hz, β -H); LRMS (FD): m/z calcd. for $\text{C}_{69}\text{H}_{69}\text{F}_8\text{N}_5\text{O}_4$ 1183.5; found 1183.5. Anal. calc. for $\text{C}_{69}\text{H}_{69}\text{F}_8\text{N}_5\text{O}_4$: C, 69.98; H, 5.87; N, 5.91. Found: C, 69.27; H, 5.73; N, 5.87%. UV-Vis (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ 411, 563, 611, 636.

5,15-Bis-(4-dodecyloxy-2,3,5,6-tetrafluorophenyl)-10-(4-aminophenyl)corrole (6). A solution of 5,15-bis-(4-dodecyloxy-2,3,5,6-tetrafluorophenyl)-10-(4-phthalimidophenyl)corrole (215 mg, 0.18 mmol) in THF (20 mL) was treated with the hydrazine hydrate (370 μL) in ethanol (5 mL). The reaction mixture was stirred for 3 h at room temperature. The mixture was concentrated and chromatographed [silica, $\text{CH}_2\text{Cl}_2/\text{heksan}$ (2:3)] affording a pure solid (185 mg, 97 %). $R_f = 0.48$ (silica; $\text{CH}_2\text{Cl}_2/\text{hexane}$, 3:2); ^1H NMR (500 MHz, CDCl_3): δ 0.90 (t, 6H, $J = 6.8$ Hz, CH_3), 1.32 (m, 28H, CH_2), 1.49 (m, 4H, CH_2), 1.64 (tt, 4H, $J_1 = 7.5$ Hz, $J_2 = 15.5$ Hz, CH_2), 1.99 (tt, 4H, $J_1 = 7.1$ Hz, $J_2 = 15.1$ Hz, CH_2), 4.54 (t, 4H, $J = 6.5$ Hz, OCH_2), 7.04, 7.96 (AA'BB', 4H, $J = 8.0$ Hz), 8.57 (br d, $J = 3.7$ Hz, 2H, β -H), 8.73 (d, 2H, $J = 4.7$ Hz, β -H), 8.74 (d, 2H, $J = 4.7$ Hz, β -H), 9.07 (d, 2H, $J = 3.8$ Hz, β -H); LRMS (FD): m/z calcd. for $\text{C}_{61}\text{H}_{67}\text{F}_8\text{N}_5\text{O}_2$ 1053.5; found 1053.7. Anal. calc. for $\text{C}_{61}\text{H}_{67}\text{F}_8\text{N}_5\text{O}_2$: C, 69.50; H, 6.41; N, 6.64. Found: C, 69.60; H, 6.41; N, 6.44%. UV-Vis (CH_2Cl_2): $\lambda_{\text{max}}/\text{nm}$ 423, 562, 621.

Corrole Trimer 1

Corrole 6 (85 mg, 0.08 mmol) and trimesylchloride (6.4 mg, 24 μmol) were dissolved in 30 mL CH_2Cl_2 (distilled and dried over CaH_2) under a nitrogen atmosphere, and stirred at 0°C . After two hours, one drop of pyridine was added to the solution. The solution was stirred overnight, allowing it to warm to room temperature. After evaporation of the solvent the residue was purified several times by size exclusion column chromatography (eluent: toluene). Yield: 42 mg (54 %) as a green blue solid.

^1H NMR (400 MHz, CDCl_3 with a droplet of DMSO- d_6): δ 10.64 (s, 3H, NH -amide), 9.09 (s, 3H, CH central benzene), 8.99 (s, broad, 6H, CH m-Ph-NH), 8.69 (s, broad, 12H, H-C3,7,13,17- β -pyrrole), 8.46 (s, broad, 6H, CH o-Ph-NH), 8.31 (s, broad, 6H, H-C9,12- β -pyrrole), 8.18 (s, broad, 6H, H-C2,18- β -pyrrole), 4.47 (t, 12H, $\text{OCH}_2\text{C}_{11}\text{H}_{23}$), 1.91 (m, 12H, $\text{OCH}_2\text{CH}_2\text{C}_{10}\text{H}_{21}$), 1.57 (m, 12H, $\text{OC}_2\text{H}_4\text{CH}_2\text{C}_9\text{H}_{19}$), 1.40 (m, 12H, $\text{OC}_3\text{H}_6\text{CH}_2\text{C}_8\text{H}_{17}$), 1.22 (m, 84H, $\text{OC}_4\text{H}_8\text{C}_7\text{H}_{14}\text{CH}_3$), 0.80 (t, 18H, $-\text{CH}_3$, $J = 6.7$ Hz), -3.03 (s, broad, NH-corrole). Maldi-TOF: M^+ : 3318.4, calculated: 3318.6. Elemental Anal. calc. for: $\text{C}_{192}\text{H}_{201}\text{F}_{24}\text{N}_{15}\text{O}_9 \cdot 3\text{H}_2\text{O}$: C, 68.37; H, 6.19; N, 6.23. Found: C, 68.49 ; H, 6.15; N, 5.69.

Atomic Force Microscopy measurements

For AFM measurements a Nanoscope IV with Dimension 3100 (Veeco / digital instruments, Santa Barbara, California) was used. Tapping in air was performed with 100 μm long standard silicon tips (NSG 10, ND-MDT, Moscow, Zelenograd, Russia) with average nominal resonant frequencies of 255 kHz and average nominal force constants of 11.5 N/m. Scanning was performed at a speed of 0.3 – 1.0 lines/s with amplitude setpoints of 1.5 – 2 V. Standard software (Nanoscope, version 6.12r3) was used for image processing (1st and 2nd order flattening) and analysis. Dropcasting experiments were carried out under an argon atmosphere at a temperature of 22 ± 0.5 °C. A droplet (3 μl) of a solution of compound **1** in chloroform or *n*-hexane was placed onto freshly cleaved mica. After evaporation of the solvent the sample was measured by tapping mode AFM.

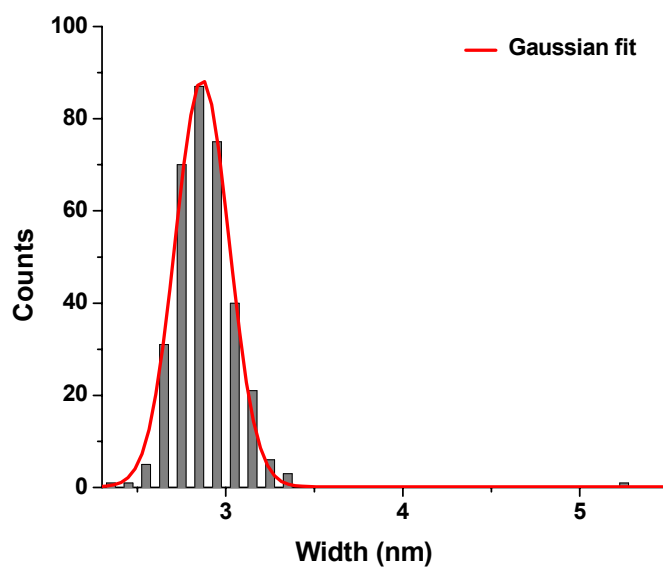


Fig. S1 Size distribution diagram of the height of the structures formed by **1** upon evaporating a 3 μL droplet of the compound in chloroform ($[\mathbf{1}] = 4 \mu\text{M}$) on mica, measured in several different domains in the AFM image.