Supporting Information for

# Complex Columnar Hexagonal Polymorphism in Supramolecular Assemblies of a Semifluorinated Electron-Accepting Napthalene Bisimide

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## 1. Materials

Phthalic anhydride, potassium *tert*-butoxide, hydrazine monohydrate, sodium azide ($NaN_3$), sodium cyanide (NaCN), benzyl chloride, $PBr_3$ (all from Acros), 3-amino-1-propanol, 1.0 M borane tetrahydrofuran complex solution, $LiAlH_4$, benzyltriethylammonium chloride, DMAP (all from Aldrich), potassium carbonate ($K_2CO_3$), Pd/C (both from Alfa Aesar) and perfluoropropyl vinyl ether (Synquest) were used as received. Triphenylphosphine ($PPh_3$) (Acros) was recrystallized from hexane prior to use. $CBr_4$ (Alfa Aesar) was recrystallized from EtOH prior to use. $CH_2Cl_2$ (Fisher, ACS reagent) was dried over $CaH_2$ and freshly distilled before used. DMF (Fisher, ACS reagent) was either dried over $CaH_2$ and freshly distilled before use, or dried over 4 Å molecular sieves for 72 h and stored over fresh 4 Å molecular sieves before use. THF and toluene (both from Fisher, ACS reagents) was refluxed over sodium and benzophenone until the solution turned purple and then distilled before used. Methyl 3,4,5-trihydroxybenzoate (**5**) was synthesized via Fisher esterification of gallic acid in MeOH with a catalytic amount of conc. $H_2SO_4$.[S1] 2,3,6,7-Tetrabromo-1,4,5,8-naphthalenetetracarboxylic acid dianhydride (**27**) was synthesized according to a literature procedure. [S2] Sodium 2,2-dicyanoethene-1,1-bis(thiolate) (**33**) was synthesized according to a literature procedure.[S3] 2-(3,4,5-Trihydroxybenzyl)isoindoline-1,3-dione (**38**) was synthesized according to a literature procedure.[S4]

## 2. Techniques

### Solution NMR

$^1$H NMR (500 MHz) and $^{13}$C NMR (125 MHz) spectra were recorded on a Bruker DRX 500 instrument. The purity of the products was determined by a combination of thin layer chromatography (TLC) and high pressure liquid chromatography (HPLC) using Perkin-Elmer Series 10 high pressure liquid chromatography with a LC-100 column oven, Nelson Analytical 900 series integrator data station and two Perkin-Elmer PL gel columns, $5 \times 10^2$ and $1 \times 10^4$ Å. THF was used as solvent with a UV detector.

### Differential Scanning Calorimetry (DSC)

Thermal transitions were measured on TA instrument 2920 modulated and Q 100 differential scanning calorimeter (DSC) integrated with a refrigerated cooling system (RCS). The heating and cooling rates were 1 or 10 $^o$C/min. The transition temperatures were measured as the maxima and minima of their

endothermic and exothermic peaks. Indium was used as standard for the calibration. An Olympus BX-51 optical polarized microscope (100× magnification) equipped with a Metler FP 82HT hot stage and Metler Toledo FP90 central processor was used to verify thermal transitions and to characterize anisotropic textures.

**Density Measurements**

For density measurements, a small mass of sample (~0.5 mg) was placed in a vial filled with water followed by ultrasonication to remove the air bubbles embedded within the sample. The sample sank to the bottom of the vial due to its high density compared with water. A saturated aqueous solution of potassium iodide (KI) was then added into the solution at ~ 0.1 g per aliquot to gradually increase the solution density. KI was added at an interval of at least 20 min to ensure equilibrium within the solution. When the sample was suspended in the middle of the solution, the density of the sample was identical to that of the solution, which was measured by a 10 mL volumetric flask.

**Matrix-Assisted Laser Desorption/Ionization Time of Flight (MALDI-TOF)**

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry was performed on PerSeptive Biosystems-Voyager-DE (Framingham, MA) mass spectrometer equipped with a nitrogen laser (337 μm) and operating in linear mode. Internal calibration was performed using Angiotensin II and Bombesin as standards. The analytical sample were obtained by mixing a THF solution of the sample (5–10 mg/mL) and the matrix (3,5-dihydroxybenzoic acid) (10 mg/mL) in a 1:1 to 1:5 v/v ratio. The prepared solution (0.5 μL) was loaded on the MALDI plate and allowed to dry at 25 $^{o}$C before the plate was inserted into the vacuum chamber of the MALDI instrument. The laser steps and voltages were adjusted depending on the molecular weight and the nature of each analyte.

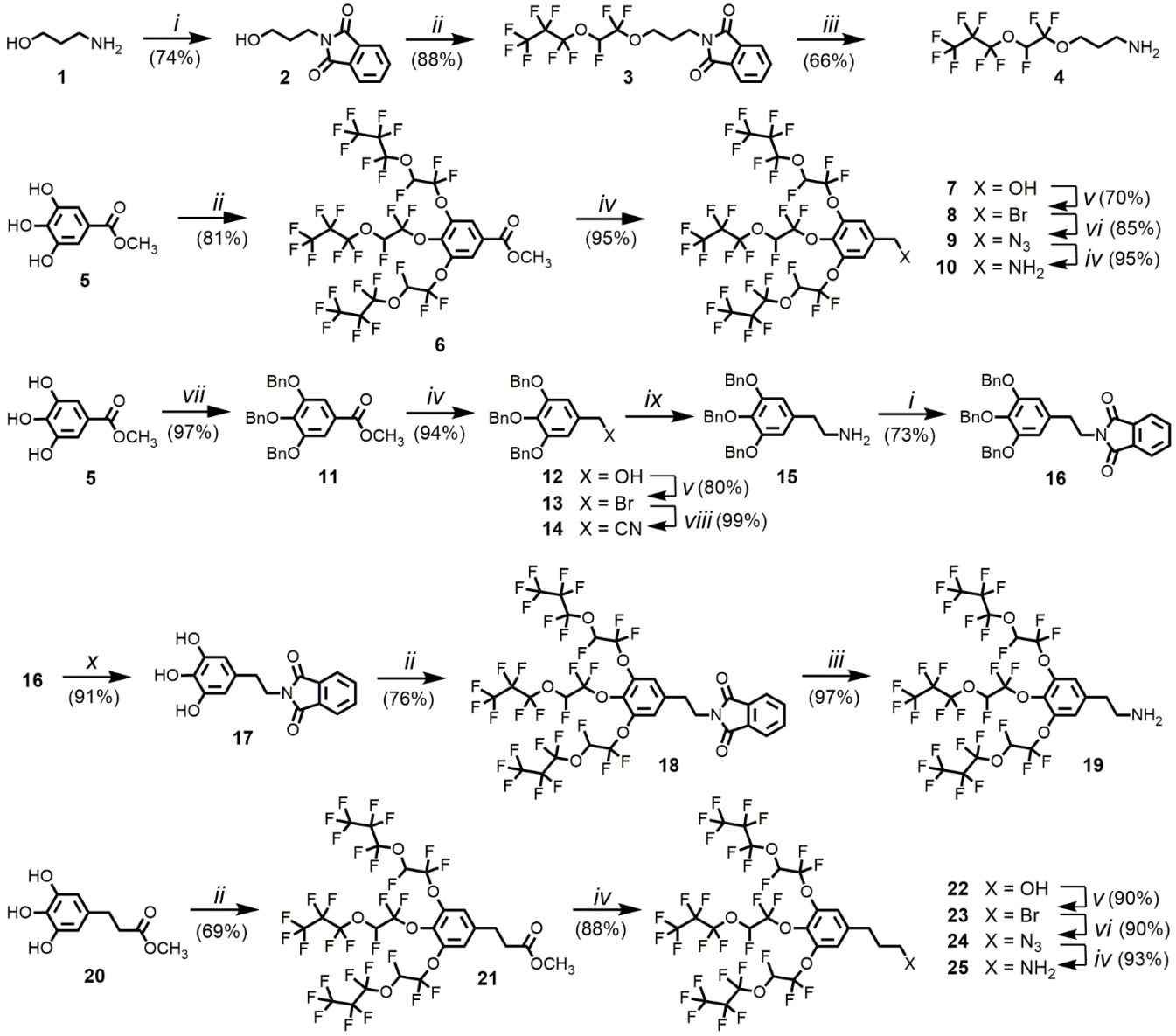
**X-ray Diffraction (XRD)**

X-ray diffraction (XRD) measurements were performed using Cu-$K_{\alpha 1}$ radiation ($\lambda$ = 1.542 Å) from a Bruker-Nonius FR-591 rotating anode X-ray source equipped with a 0.2 × 0.2 mm$^2$ filament and operated at 3.4 kW. Osmic Max-Flux optics and triple pinhole collimation were used to obtain a highly collimated beam with a 0.3 × 0.3 mm$^2$ spot on a Bruker-AXS Hi-Star multiwire area detector. To minimize attenuation and background scattering, an integral vacuum was maintained along the length of the flight tube and within the sample chamber. Samples were held in quartz capillaries (0.7–1.0 mm in diameter), mounted in a temperature-controlled oven (temperature precision: ± 0.1 °C, temperature range from –120 °C to 270 °C). The distance between the sample and the detector was 11.0 cm for wide angle diffraction experiments and 54.0 cm for intermediate angle diffraction experiments. Aligned samples for fiber XRD experiments were prepared using a custom made extrusion device.[S4] The

powdered sample (~10 mg) was heated inside the extrusion device. After slow cooling, the fiber was extruded in the liquid crystal phase and cooled to 23 °C. Typically, the aligned samples have a thickness of 0.3–0.7 mm and a length of 3–7 mm. All XRD measurements were done with the aligned sample axis perpendicular to the beam direction. Primary XRD analysis was performed using Datasqueeze (version 3.0). Molecular models were built and visualized using Materials Studio (Accelrys). For energy minimization the Forcite module and Universal forcefield were used.

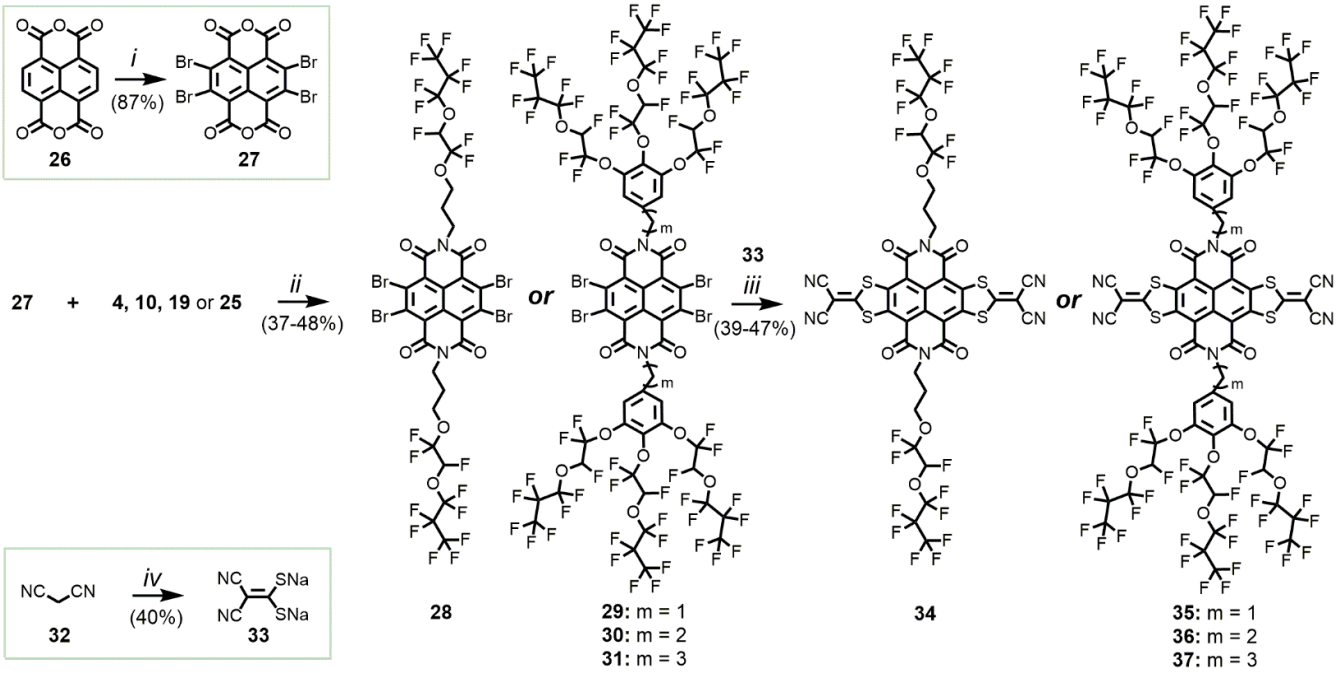
## 3. Synthesis

**Supporting Scheme SS1. Synthesis of Semifluorinated Linear and Minidendritic Precursors with *m* = 1, 2, 3**



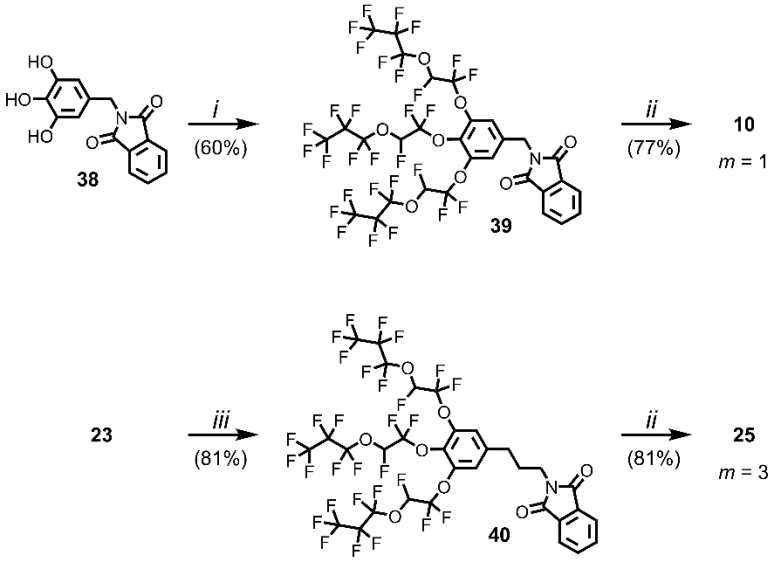

**Reagents and conditions**: (i) phthalic anhydride, DMAP (120 °C); (ii) $^{t}$BuOK, $CF_2=CFOC_3F_7$, DMF; (iii) $NH_2$-$NH_2.H_2O$, EtOH-THF (reflux); (iv) $LiAlH_4$, THF (0 °C); (v) $CBr_4$, $PPh_3$, THF (0 °C); (vi) $NaN_3$, DMF; (vii) BnCl, $K_2CO_3$, $CH_3CN$ (80 °C); (viii) NaCN, benzyltriethylammonium chloride, DMF; (ix) 1 M $BH_3$-THF, THF (reflux); (x) $H_2$, Pd/C, THF-EtOH (25 °C)

**Supporting Scheme SS2. The Synthesis of the Semifluorinated Linear and Dendronized NBI Derivatives 34, 35, 36, and 37**

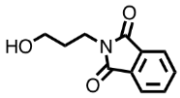



**Reagents and conditions**: (i) Dibromoisocyanuric acid, oleum, 3 h (RT) (ii) $CH_3COOH$, DMF-toluene, 30 min (100 $^oC$) then $PBr_3$, 12 h (reflux); (iii) **33**, THF, 1 h (50 $^oC$); (iv) $CS_2$, NaOH, MeOH, 1 h (RT).

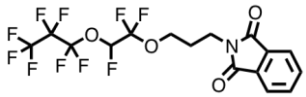
**Supporting Scheme SS3. Alternative Synthesis of Semifluorinated Amines 10 and 25**



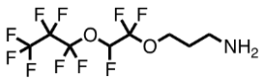

**Reagents and conditions**: (i) $^tBuOK$, $CF_2=CFOC_3F_7$, DMF, 48 h (RT) (ii) $NH_2NH_2.H_2O$, EtOH, 3 h (reflux); (iii) potassium phthalimide, DMF, 12 h (100 °C).



**3-Hydroxypropylphthalimide (2).** A mixture of 3-aminopropan-1-ol (7.5 g, 0.1 mol), phthalic anhydride (14.8 g, 0.1 mol), and DMAP (1.22 g, 0.01 mol) was heated at 120 °C for 2 h. The mixture was then cooled to room temperature, diluted with $CH_2Cl_2$ and washed with water. The combined organics were dried ($MgSO_4$), filtered and dried *in vacuo*. The resultant residue was purified by column chromatography (silica gel, MeOH/$CH_2Cl_2$, 1:15) to afford a white solid (15.3 g, 74%). Purity (HPLC), 99+%. $^1$H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 7.85–7.84 (m, 2H), 7.73 – 7.71 (m, 2H), 3.85 (t, *J* = 6.5 Hz, 2H), 3.61 (t, *J* = 6.5 Hz, 2H), 1.88 (m, 2H). $^{13}$C NMR ($CDCl_3$, 500 MHz): δ (ppm) = 169.1, 134.3, 132.1, 123.5, 59.1, 34.3, 31.4. HRMS calc. for $[C_{11}H_{11}NNaO_3]^{+:}$ 208.20; found m/z: 228.06 $[M+Na]^+$.

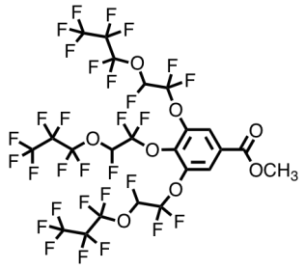


**3-(1,1,2-Trifluoro-2-(perfluoropropoxy)ethoxy)propylphthalimide (3).** Perfluoropropyl vinyl ether (7.13 g, 26.8 mmol) was added to a sealed (with septum) round-bottomed flask containing a magnetic stirring bar under inert atmosphere. Compound **2** (5 g, 24.4 mmol) and dry DMF (50 mL) were subsequently added at 0 ºC. When all solid had dissolved, potassium *tert*-butoxide (0.28 g, 2.44 mmol) was quickly added to the reaction mixture. The temperature was maintained at 0 °C for 2 h. The reaction mixture was allowed to warm to room temperature whereupon it was stirred for 48 h. The reaction mixture was poured into ice-cold water (300 mL) containing concentrated hydrochloric acid (3 mL) and extracted with ethyl acetate. The combined organics were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residual oil was purified by column chromatography (silica gel, EtOAc/hexanes, 1/6) to yield a clear oil (10.1 g, 88%). Purity (HPLC), 99+%. $^1$H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 7.86–7.83 (m, 2H), 7.73–7.70 (m, 2H), 5.83 (d, $^2J$ = 59.5 Hz, 1H, -CHF), 4.04 (t, *J* = 6.3 Hz, 2H), 3.79 (t, *J* = 7.0 Hz, 2H), 2.08 (m, 2H). $^{13}$C NMR ($CDCl_3$, 500 MHz): δ (ppm) = 168.3, 134.2, 132.2, 123.4, 120.9–104.4(-$CF_2$-), 99.4–96.7 (-CHF-), 62.4, 34.7, 28.1. HRMS calc. for $[C_{16}H_{11}F_{10}NNaO_4]^{+:}$ 494.24; found m/z: 494.04 $[M+Na]^+$.

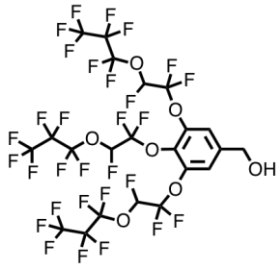


**3-(1,1,2-Trifluoro-2-(perfluoropropoxy)ethoxy)propan-1-amine (4).** To a solution of **3** (4.7 g, 10 mmol) in ethanol/THF (2:1, v/v, 90 mL) was added hydrazine hydrate (2.5 g, 50 mmol). The mixture was refluxed for 3 h resulting in the formation of a white precipitate. The reaction mixture was cooled to room temperature, concentrated *in vacuo*, and diluted with THF. Filtration of the white solid through

Celite and concentration of the solution gave the desired amine, which was used without further purification, as a yellow oil (2.24 g, 66%). $^{1}$H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 5.86 (d, $^{2}J$ = 59.5 Hz, 1H, -CHF), 4.07 (t, $J$ = 6.3 Hz, 2H), 2.81 (t, $J$ = 6.8 Hz, 2H), 1.81 (m, 2H).

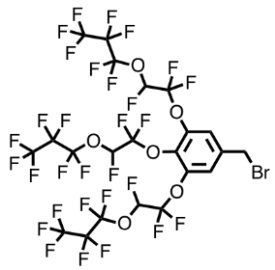


**Methyl 3,4,5-tris(1,1,2-trifluoro-2-(perfluoropropoxy)ethoxy)benzoate (6).** Perfluoropropyl vinyl ether (13.0 g, 48.9 mmol) was added to a sealed (with septum) round-bottomed flask containing a magnetic stirring bar under inert atmosphere. The reaction was cooled to 0 °C whereupon methyl 3,4,5-trihydroxybenzoate (**5**) (3.0 g, 16.3 mmol) and dry DMF (50 mL) were added. When all solid had dissolved, potassium *tert*-butoxide (0.55 g, 4.9 mmol) was quickly added to the reaction mixture. The temperature was maintained at 0 °C for 2 h. The reaction mixture was allowed to warm to room temperature whereupon it was stirred for 48 h. The solution was poured into ice-cold water (500 mL) containing concentrated hydrochloric acid (5 mL) and extracted with ethyl acetate. The combined organics were washed with water, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residual oil was purified by column chromatography (silica gel, EtOAc/hexanes, 1:9) to give the product as an oil (12.9 g, 81%). Purity (HPLC), 99+%. $^{1}$H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 8.01 (s, 2H), 6.08 (d, $^{2}J$ = 53.5 Hz, 3H, -CHF), 3.97 (s, 3H). $^{13}$C NMR ($CDCl_3$, 500 MHz): δ (ppm) = 164.0, 143.6, 136.8, 130.4, 121.7, 120.9–104.1 (-$CF_2$-), 99.1–96.5 (-CHF-), 53.3. MALDI-TOF MS calc. for $[C_{23}H_8AgF_{30}O_8]^+$: 1088.88; found m/z: 1088.72 $[M+Ag]^+$.

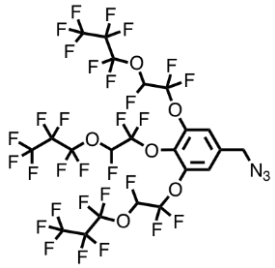


**(3,4,5-Tris(1,1,2-trifluoro-2-(perfluoropropoxy)ethoxy)phenyl)methanol (7).** To a suspension of $LiAlH_4$ (1.3 g, 34.2 mmol) in dry THF (20 mL) at 0 °C under nitrogen atmosphere was added dropwise a solution of **6** (16.8 g, 17.1 mmol) in 30 mL of dry THF. After the addition was completed, the reaction mixture was stirred at 0 °C for 2 h. The reaction mixture was quenched by successive dropwise addition of 2 mL of $H_2O$ (2 mL), NaOH solution (15% aq., 2 mL) and $H_2O$ (10 mL). The granular salts were

filtered through Celite and washed with THF. Evaporation of the solvent *in vacuo* produced the product as a colorless oil (15.5 g, 95%) which was used in the next reaction without further purification. Purity (HPLC), 99+%. $^{1}$H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 7.35 (s, 2H), 6.06 (d, $^{2}J$ = 53.5 Hz, 3H, -CHF), 4.75 (s, 2H). $^{13}$C NMR ($CDCl_3$, 500 MHz): δ (ppm) = 143.5, 141.9, 132.1, 118.3, 120.7–104.4 (-$CF_2$-), 99.2–96.5 (-CHF-), 63.7. MALDI-TOF MS calc. for $[C_{22}H_8AgF_{30}O_7]^+$: 1060.88; found m/z: 1062.16 $[M+Ag]^+$.

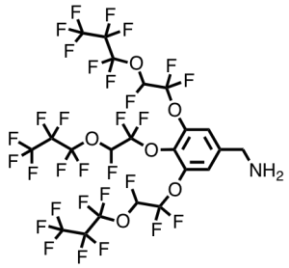


**1,2,3-Tris(1,1,2-trifluoro-2-(perfluoropropoxy)ethoxy)-5-(bromomethyl) benzene (8).** A solution of **7** (9.54 g, 10.0 mmol) and $CBr_4$ (4.31 g, 13.0 mmol) in dry THF (30 mL) was cooled to 0 °C, whereupon a solution of $PPh_3$ (3.40 g, 13.0 mmol) in dry THF (20 mL) was added dropwise under $N_2$. The reaction mixture was stirred at 0 °C for 2 h. The mixture was poured into hexane and the salts were removed by filtration. The filtrate was dried *in vacuo* and the crude product was purified by column chromatography (silica gel, EtOAc/hexanes, 1/20) to afford the pure product as a colorless oil (7.14 g, 70%). Purity (HPLC), 99+%. $^{1}$H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 7.37 (s, 2H), 6.06 (d, $^{2}J$ = 53.5 Hz, 3H, -CHF), 4.44 (s, 2H). $^{13}$C NMR ($CDCl_3$, 500 MHz): δ (ppm) = 143.3, 138.4, 132.8, 120.9, 120.7–104.2 (-$CF_2$-), 98.9–96.3 (-CHF-), 30.5. MALDI-TOF MS calc. for $[C_{22}H_{7Br}F_{30}NaO_6]^+$: 1038.88; found m/z: 1036.13 $[M+Na]^+$.



**5-(Azidomethyl)-1,2,3-tris(1,1,2-trifluoro-2-(perfluoropropoxy)ethoxy) benzene (9).** To a solution of **8** (7.14 g, 7.0 mmol) in DMF (30 mL) was added sodium azide (1.37 g, 21.0 mmol). The resulting mixture was stirred at room temperature for 2 h. After TLC indicated complete conversion, the reaction was diluted with ethyl acetate and washed with water. The aqueous layer was further washed with ethyl acetate. The combined organics were washed with brine, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude product was purified by column chromatography (silica gel, EtOAc/hexanes, 1/20) to

give the corresponding azide **7** as a colorless oil (5.83 g, 85%). Purity (HPLC), 99+%. $^{1}$H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 7.30 (s, 2H), 6.06 (d, $^{2}J$ = 56.5 Hz, 3H, -CHF), 4.45 (s, 2H). $^{13}$C NMR ($CDCl_3$, 500 MHz): δ (ppm) = 143.8, 136.8, 132.9, 119.7, 120.7–104.5 (-$CF_2$-), 99.2–96.5 (-CHF-), 53.5. MALDI-TOF MS calc. for $[C_{22}H_7AgF_{30}N_3O_6]^+$: 1085.89; found m/z: 1086.90 $[M+Ag]^+$.

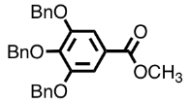


**(3,4,5-Tris(1,1,2-trifluoro-2-(perfluoropropoxy)ethoxy)phenyl)methanamine (10)**.

Method 1 (Supporting Scheme SS1): To a suspension of $LiAlH_4$ (0.43 g, 11.2 mmol) in dry THF (20 mL) at 0 °C was added a solution of **9** (5.5 g, 5.6 mmol) in dry THF (30 mL) dropwise under nitrogen atmosphere. The reaction mixture was stirred at 0 °C for 2 h. The reaction was quenched by successive dropwise addition of $H_2O$ (2 mL), NaOH solution (15% aq., 2 mL) and $H_2O$ (6 mL). The granular salts were filtered through Celite and washed with THF. The solvent was fully evaporated to produce the desired amine which was used in the next step without further purification (5.1 g, 95%).

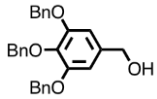
Method 2 (Supporting Scheme SS3): To a solution of compound **39** (6.85 g, 6.32 mmol) in ethanol (200 proof, 70 mL) was added hydrazine hydrate (64% hydrazine, 3.07 mL, 63.2 mmol). The mixture was refluxed for 3 h resulting in the formation of a white precipitate. The reaction mixture was cooled to room temperature and diluted with diethyl ether. Filtration of the white solid through Celite and concentration of the solution gave the desired amine, which was used in the next step without further purification, as a yellow oil (4.62 g, 77%).

$^{1}$H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 7.34 (s, 2H), 6.06 (d, $^{2}J$ = 56.0 Hz, 3H, -CHF), 3.95 (s, 2H).

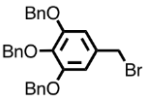


**Methyl 3,4,5-tris(benzyloxy)benzoate (11).** To a solution of benzyl chloride (12.0 g, 95.0 mmol) and potassium carbonate (16.9 g 122.2 mmol) in acetonitrile (150 mL) was added methyl 3,4,5-trihydroxy benzoate (**5**) (5.0 g, 27.2 mmol). The mixture was refluxed at 80 °C under nitrogen atmosphere for 48 h. After cooling to room temperature, the solution was filtered and concentrated by evaporating the solvent. The crude product was dissolved in 150 mL $CH_2Cl_2$ and extracted with brine (200 mL) three times. The organic phase was then dried over magnesium sulfate, isolated by evaporating the solvent, purified by column chromatography (silica gel, $CH_2Cl_2$/hexanes, 2/1). The solvent was removed under reduced

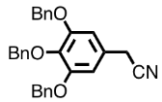
pressure to produce the pure product as a white solid (12.0 g, 97%). Purity (HPLC), 99+%. $^{1}$H NMR ($d_6$-acetone, 500 MHz): δ (ppm) = 7.54–7.26 (m, 17H), 5.21 (s, 4H), 5.13 (s, 2H), 3.85 (s, 3H). $^{13}$C NMR ($d_6$-acetone, 500 MHz): δ (ppm) = 166.8, 153.6, 143.2, 138.8, 138.1, 129.3, 129.2, 129.0, 128.8, 128.7, 128.6, 126.3, 109.6, 75.5, 71.7, 52.4. HRMS calc. for $[C_{29}H_{26}NaO_5]^+$: 477.50; found m/z: 477.17 $[M+Na]^+$ .




**(3,4,5-Tris(benzyloxy)phenyl)methanol (12).** A solution of **11** (11.9 g, 26.2 mmol) in dry THF (50 mL) was added dropwise to a stirred suspension of $LiAlH_4$ (1.74 g, 45.8 mmol) in dry THF (20 mL) at 0 °C under nitrogen atmosphere. After the addition was complete, the reaction mixture was stirred at 0 °C for 2 h. Excess hydride was quenched by successive dropwise addition of $H_2O$ (2 mL), NaOH solution (15% aq., 2 mL) and $H_2O$ (6 mL). The granular salts were filtered and washed with THF. Evaporation of the solvent gave the crude product, which was recrystallized from MeOH to afford pure product as a white solid (10.5 g, 94%). Purity (HPLC), 99+%. $^{1}$H NMR ($d_6$-acetone, 500 MHz): δ (ppm) = 7.50–7.25 (m, 15H), 6.82 (s, 2H), 5.14 (s, 4H), 5.02 (s, 2H), 4.56 (s, 2H). $^{13}$C NMR ($d_6$-acetone, 500 MHz): δ (ppm) = 153.7, 139.4, 139.3, 138.6, 137.9, 129.2, 129.1, 128.9, 128.6, 128.43, 128.40, 106.6, 75.5, 71.5, 64.7. HRMS calc. for $[C_{28}H_{26}NaO_4]^+$: 449.49; found m/z: 449.17 $[M+Na]^+$.

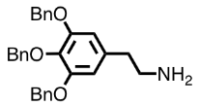



**1,2,3-Tris(benzyloxy)-5-(bromomethyl)benzene (13).** A solution of $PPh_3$ (8.2 g, 31.1 mmol) in dry THF (20 mL) was added dropwise to a solution of **12** (10.2 g, 23.9 mmol) and $CBr_4$ (10.3 g, 31.1 mmol) in dry THF (40 mL) at 0 °C under nitrogen atmosphere. After the addition was complete, the reaction mixture was stirred at 0 °C for 3 h. The reaction mixture was poured into methanol (600 mL) and kept in the refrigerator for 5 h. The white precipitate was filtered and dried under vacuum to afford a white solid (9.3 g, 80%). $^{1}$H NMR ($d_6$-acetone, 500 MHz): δ (ppm) = 7.53–7.25 (m, 15H), 6.95 (s, 2H), 5.17 (s, 4H), 5.03 (s, 2H), 4.59 (s, 2H). $^{13}$C NMR ($d_6$-acetone, 500 MHz): δ (ppm) = 153.7, 139.2, 138.2, 134.7, 129.3, 129.1, 128.9, 128.7, 128.6, 128.5, 109.5, 75.5, 71.6, 35.1. HRMS calc. for $[C_{28}H_{25}BrNaO_3]^+$: 512.39; found m/z: 513.09 $[M+Na]^+$ .

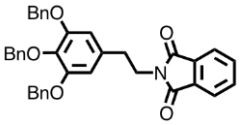



**2-(3,4,5-Tris(benzyloxy)phenyl)acetonitrile (14).** Compound **13** (9.5 g, 19.4 mmol) was dissolved in DMF (50 mL). Sodium cyanide (2.1 g, 42.7 mmol) and benzyltriethylammonium chloride (0.2 g, 0.9

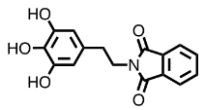
mmol) were added. The mixture was stirred at room temperature for 1 h. The reaction mixture was poured into water and extracted with ethyl acetate. The combined organics were washed with water, dried ($MgSO_4$) and concentrated *in vacuo*. The crude product was recrystallized from a methanol-acetone mixture to afford pure product as a white solid (8.4 g, 99%). $^1$H NMR ($d_6$-acetone, 500 MHz): δ (ppm) = 7.53–7.26 (m, 15H), 6.86 (s, 2H), 5.17 (s, 4H), 5.03 (s, 2H), 3.87 (s, 2H). $^{13}$C NMR ($d_6$-acetone, 500 MHz): δ (ppm) = 154.1, 139.1, 138.6, 138.2, 129.3, 129.1, 128.9, 128.7, 128.6, 128.5, 127.8, 108.5, 75.5, 71.7, 23.5. HRMS calc. for $[C_{29}H_{25}NNaO_3]^+$: 458.50; found m/z: 458.18 $[M+Na]^+$ .




**2-(3,4,5-Tris(benzyloxy)phenyl)ethanamine (15).** 1.0 M Borane tetrahydrofuran complex solution (115.7 mL, 115.7 mmol) was added dropwise to a solution of benzyl cyanide **14** (8.4 g, 19.3 mmol) in dry THF (50 mL) at 0 °C. After addition was complete, the mixture was refluxed under nitrogen for 20 h. The solution was then cooled to 0 °C whereupon excess borane was quenched by cautious addition of methanol. The mixture was concentrated *in vacuo*. The residual oil was taken up into methanol and concentrated again (repeated twice more) to give the oily amine which was used in the next reaction without further purification.

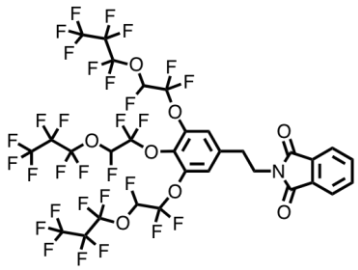



**2-(3,4,5-Tris(benzyloxy)phenethyl)phthalimide (16).** A mixture of compound **15** (as prepared in the previous reaction, theoretical yield = 19.3 mmol), phthalic anhydride (2.86 g, 19.3 mmol), and DMAP (0.24 g, 1.93 mmol) was refluxed at 120 °C for 3 h. The mixture was then cooled to room temperature and concentrated *in vacuo*. The crude product was purified by column chromatography (silica gel, $CH_2Cl_2$) to afford pure product as a white solid (8.0 g, 73%). $^1$H NMR ($d_6$-acetone, 500 MHz): δ (ppm) = 7.86–7.82 (m, 4H), 7.47–7.24 (m, 15H), 6.69 (s, 2H), 5.04 (s, 4H), 4.97 (s, 2H), 3.91 (t, $J$ = 7.3 Hz, 2H), 2.94 (t, $J$ = 7.3 Hz, 2H). $^{13}$C NMR ($d_6$-acetone, 500 MHz): δ (ppm) = 168.6, 153.8, 139.4, 138.5, 137.9, 135.1, 135.0, 133.2, 129.2, 129.1, 128.9, 128.6, 128.5, 128.4, 123.8, 109.1, 75.5, 71.6, 39.7, 35.1. HRMS calc. for $[C_{37}H_{31}NNaO_5]^+$: 592.64; found m/z: 592.21 $[M+Na]^+$ .

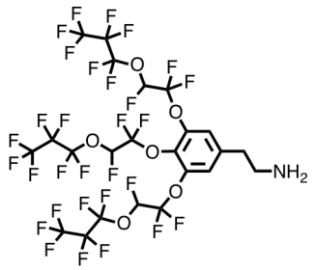



**2-(3,4,5-Trihydroxyphenethyl)phthalimide (17).** In a 500 mL round-bottomed flask, compound **16** (8.8 g, 15.4 mmol) and Pd/activated carbon (10% Pd/C, 0.6 g) were suspended in THF/EtOH (1:1 v/v,

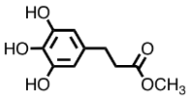
100 mL). After flushing with $H_2$, hydrogenation ($H_2$ balloon) was continued for 48 h under stirring. When the reaction was complete by TLC, the mixture was filtered through Celite, washing with THF. The solvent was evaporated *in vacuo* to yield the crude product, which was recrystallized from THF/hexane to afford pure product as a yellow solid (4.2 g, 91%). Purity (HPLC), 99+%. $^1$H NMR ($d_6$-acetone, 500 MHz): δ (ppm) = 7.82 (s, 4H), 6.28 (s, 2H), 3.79 (t, *J* = 7.5 Hz, 2H), 2.77 (t, *J* = 6.5 Hz, 2H). $^{13}$C NMR ($d_6$-acetone, 500 MHz): δ (ppm) = 168.6, 146.6, 134.9, 133.1, 132.2, 130.4, 123.7, 108.5, 40.2, 34.7. HRMS calc. for $[C_{16}H_{13}NNaO_5]^+$: 322.27; found m/z: 322.07 $[M+Na]^+$.



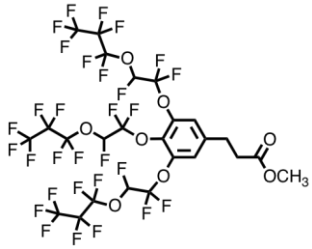
**2-(3,4,5-Tris(1,1,2-trifluoro-2-(perfluoropropoxy)ethoxy)phenethyl) phthalimide (18).** Perfluoropropyl vinyl ether (11.7 g, 44.1 mmol) was added to a sealed (with septum) round-bottom flask containing a magnetic stirring bar under inert atmosphere. The reaction was cooled to 0 °C, whereupon compound **17** (4.0 g, 13.4 mmol) and dry DMF (50 mL) were added. When all solid had dissolved, potassium *tert*-butoxide (0.45 g, 4.0 mmol) was quickly added to the reaction mixture. The temperature was maintained at 0 °C for 2 h. The reaction mixture was allowed to warm to room temperature whereupon it was stirred for 48 h. The solution was poured into ice-cold water (500 mL) containing concentrated hydrochloric acid (5 mL) and extracted with ethyl acetate. The combined organics were washed with water, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residual oil was purified by column chromatography (silica gel, EtOAc/hexanes, 1:6) to give the product as a white solid (11.1 g, 76%). Purity (HPLC), 99+%. $^1$H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 7.84–7.80 (m, 2H), 7.72–7.69 (m, 2H), 7.19 (s, 2H), 6.03 (d, $^2J$ = 53.5 Hz, 3H, -CHF), 3.95 (t, *J* = 7.3 Hz, 2H), 3.05 (t, *J* = 7.3 Hz, 2H). $^{13}$C NMR ($CDCl_3$, 500 MHz): δ (ppm) = 168.1, 143.4, 139.2, 134.3, 132.0 123.5, 120.9, 120.7–104.4 (-$CF_2$-), 99.1–96.5 (-CHF-), 38.5, 34.3. MALDI-TOF MS calc. for $[C_{31}H_{13}F_{30}NNaO_8]^+$: 1120.01; found m/z: 1119.05 $[M+Na]^+$.



**2-(3,4,5-Tris(1,1,2-trifluoro-2-(perfluoropropoxy)ethoxy)phenyl) ethanamine (19).** To a solution of compound **18** (6.0 g, 5.47 mmol) in ethanol/THF (2:1 v/v, 90 mL) was added hydrazine hydrate (1.37 g, 27.3 mmol). The mixture was refluxed for 3 h resulting in the formation of a white precipitate. The reaction mixture was cooled to room temperature, concentrated *in vacuo*, and diluted with THF. Filtration of the white solid through Celite and concentration of the solution gave the desired amine, which was used in the next step without further purification, as a yellow oil (5.13 g, 97%). $^{1}$H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 7.19 (s, 2H), 6.06 (d, $^{2}J$ = 53.4 Hz, 3H, -CHF), 3.02 (t, $J$ = 6.9 Hz, 2H), 2.79 (t, $J$ = 6.9 Hz, 2H).

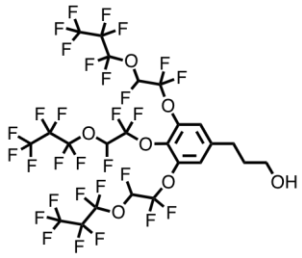


**Methyl 3-(3,4,5-trihydroxyphenyl)propionate (20).** This compound was synthesized according to a literature procedure. [S5]

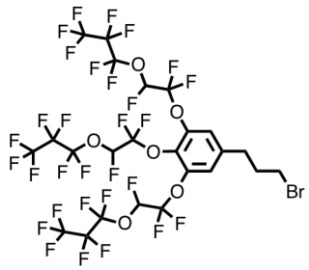


**Methyl 3-(3,4,5-tris(1,1,2-trifluoro-2-(perfluoropropoxy)ethoxy) phenyl)propanoate (21).** Perfluoropropyl vinyl ether (17.6 g, 66.0 mmol) was added to a sealed (with septum) round-bottomed flask (magnetic spinbar) under inert atmosphere. The reaction was cooled to 0 °C, and compound **20** (4.25 g, 20.0 mmol) and dry DMF (50 mL) were subsequently added. When all solid had dissolved, potassium *tert*-butoxide (0.74 g, 6.6 mmol) was quickly added to the reaction mixture. The temperature was maintained at 0 °C for 2 h. The reaction mixture was allowed to warm to room temperature whereupon it was stirred for 48 h. The solution was poured into ice-cold water (500 mL) containing concentrated hydrochloric acid (5 mL) and extracted with ethyl acetate. The combined organics were washed with water, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residual oil was purified by column chromatography (silica gel, EtOAc/hexanes, 1:9) to give the product as a colorless oil (13.9 g,

69 %). Purity (HPLC), 99+%. $^{1}$H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 7.18 (s, 2H), 6.05 (d, $^{2}J$ = 56.0 Hz, 3H, -CHF), 3.68 (s, 3H), 2.99 (t, $J$ = 7.5 Hz, 2H), 2.66 (t, $J$ = 7.5 Hz, 2H). $^{13}$C NMR ($CDCl_3$, 500 MHz): δ (ppm) = 172.5, 143.3, 141.6, 131.5, 120.6, 119.2–104.1 (-$CF_2$-), 99.1–96.5 (-CHF-), 52.0, 35.0, 30.6. MALDI-TOF MS calc. for $[C_{25}H_{12}AgF_{30}O_8]^+$: 1116.91; found m/z: 1118.06 $[M+Ag]^+$.

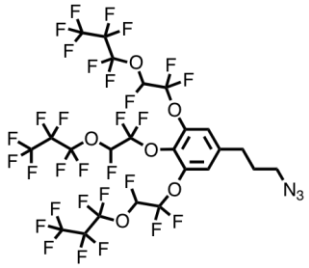


**3-(3,4,5-Tris(1,1,2-trifluoro-2-(perfluoropropoxy)ethoxy)phenyl)propan-1-ol (22).** A solution of **21** (13.5 g, 13.4 mmol) in dry THF (50 mL) was added to a suspension of $LiAlH_4$ (1.0 g, 26.7 mmol) in dry THF (20 mL), dropwise at 0 °C. The reaction mixture was stirred at 0 °C for 2 h and quenched by successive dropwise addition of $H_2O$ (2 mL), NaOH solution (15% aq., 2 mL) and $H_2O$ (5 mL). The granular salts were filtered and washed with THF. Evaporation of the solvent afforded crude product which was purified by column chromatography (silica gel, EtOAc/hexanes, 1:3) to afford the pure product as a colorless oil (11.6 g, 88 %). Purity (HPLC), 99+%. $^{1}$H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 7.17 (s, 2H), 6.06 (d, $^{2}J$ = 53.5 Hz, 3H, -CHF), 3.71 (t, $J$ = 7.7 Hz, 2H), 2.78 (t, $J$ = 7.4 Hz, 2H), 1.90 (m, 2H). $^{13}$C NMR ($CDCl_3$, 500 MHz): δ (ppm) = 143.2, 143.1, 131.2, 120.7, 119.2–104.1 (-$CF_2$-), 99.1–96.5 (-CHF-), 61.6, 33.6, 31.9. MALDI-TOF MS calc. for $[C_{24}H_{12}AgF_{30}O_7+]^+$: 1088.92; found m/z: 1088.01 $[M+Ag]^+$.

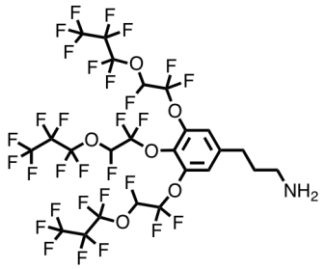


**1,2,3-Tris(1,1,2-trifluoro-2-(perfluoropropoxy)ethoxy)-5-(3-bromopropyl)benzene (23).** A solution of **22** (11.0 g, 11.2 mmol) and $CBr_4$ (4.83 g, 14.6 mmol) in dry THF (40 mL) was cooled to 0 °C, whereupon a solution of $PPh_3$ (3.82 g, 14.6 mmol) in dry THF (20 mL) was added dropwise under $N_2$. The reaction mixture was stirred at 0 °C for 2 h. After the reaction was complete (TLC control), hexane was added to precipitate the triphenylphosphine oxide formed as a by-product, which was removed by filtration. The filtrate was dried *in vacuo* and the crude product was purified by column chromatography (silica gel, EtOAc/hexanes, 1:20) to afford the pure product as a colorless oil (10.6 g, 90 %). Purity

(HPLC), 99+%. $^{1}$H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 7.17 (s, 2H), 6.06(d, $^{2}J$ = 53.5 Hz, 3H, -CHF), 3.41 (t, $J$ = 7.3 Hz, 2H), 2.85 (t, $J$ = 7.3 Hz, 2H), 2.18 (m, 2H). $^{13}$C NMR ($CDCl_3$, 500 MHz): δ (ppm) = 143.4, 141.7, 131.5, 120.8, 119.2–104.1 (-$CF_2$-), 99.2–96.6 (-CHF-), 33.8, 33.5, 32.2. MALDI-TOF MS calc. for $[C_{24}H_{11}AgBrF_{30}O_6+]^+$: 1150.83; found m/z: 1151.26 $[M+Ag]^+$.



**1,2,3-Tris(1,1,2-trifluoro-2-(perfluoropropoxy)ethoxy)-5-(3-azidopropyl) benzene (24).** To a solution of **23** (10.0 g, 9.57 mmol) in DMF (30 mL) was added sodium azide (1.87 g, 28.7 mmol). The resulting mixture was stirred at room temperature for 3 h. After TLC indicated complete conversion, the reaction was diluted with ethyl acetate and washed with water. The aqueous layer was further washed with ethyl acetate. The combined organics were washed with brine, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude product was purified by column chromatography (silica gel, EtOAc/hexanes, 1:20) to give the desired product as a colorless oil (8.67 g, 90%). Purity (HPLC), 99+%. $^{1}$H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 7.15 (s, 2H), 6.06 (d, $^{2}J$ = 53.5 Hz, 3H, -CHF), 3.35 (t, $J$ = 6.5 Hz, 2H), 2.76 (t, $J$ = 7.8 Hz, 2H), 1.92 (m, 2H). $^{13}$C NMR ($CDCl_3$, 500 MHz): δ (ppm) = 143.3, 142.0, 131.4, 120.6, 119.2–104.1 (-$CF_2$-), 99.2–96.5 (-CHF-), 50.5, 32.7, 30.1. MALDI-TOF MS calc. for $[C_{24}H_{11}AgF_{30}N_3O_6+]^+$: 1113.92; found m/z: 1114.64 $[M+Ag]^+$.



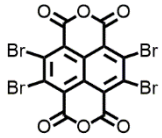
**3-(3,4,5-Tris(1,1,2-trifluoro-2-(perfluoropropoxy)ethoxy)phenyl)propan-1-amine (25).**

Method 1 (Supporting Scheme SS1): To a suspension of $LiAlH_4$ (0.63 g, 16.5 mmol) in dry THF (20 mL) at 0°C was added a solution of compound **24** (8.3 g, 8.24 mmol) in dry THF (30 mL) dropwise under nitrogen atmosphere. After addition was complete, the reaction mixture was allowed to warm to room temperature whereupon it was stirred for 3 h. The reaction was quenched by successive dropwise addition of $H_2O$ (2 mL), NaOH solution (15% aq., 2 mL) and $H_2O$ (6 mL). The granular salts were

filtered through Celite and washed with THF. The solvent was fully evaporated to produce the desired amine used without further purification (7.5 g, 93%).

Method 2 (Supporting Scheme SS3): To a solution of compound **40** (0.28 g, 0.25 mmol) in ethanol (200 proof, 5 mL) was added hydrazine hydrate (64% hydrazine, 0.12 mL, 2.5 mmol). The mixture was refluxed for 3 h resulting in the formation of a white precipitate. The reaction mixture was cooled to room temperature and diluted with diethyl ether. Filtration of the white solid through Celite and concentration of the solution gave the desired amine, which was used in the next step without further purification, as a yellow oil (0.20 g, 81%).

$^1$H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 7.16 (s, 2H), 6.06 (d, $^2J$ = 53.4 Hz, 3H, -CHF), 2.79 (t, $J$ = 7.4 Hz, 2H), 2.72 (t, $J$ = 7.4 Hz, 2H), 1.84 (m, 2H).



**2,3,6,7-Tetrabromo-1,4,5,8-naphthalenetetracarboxylic acid dianhydride (27).** This compound was synthesized according to a literature procedure. [S2]

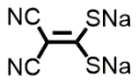
**General Procedure for the Synthesis of Tetrabromonaphthalene Bisimides (TBNBI).** Tetrabromonaphthalene dianhydride **27** (1 eq.), the corresponding amine (2.2 eq.), and acetic acid (5 eq.) in dry toluene (20 mL) and dry DMF (2 mL) were stirred under a nitrogen atmosphere at 100 °C for 30 min. $PBr_3$ (10 eq.) was added to this solution, which was then refluxed for 12 h. The mixture was cooled to room temperature, poured into water and extracted with toluene. The combined organics were concentrated *in vacuo* to afford crude product which was purified by column chromatography.

**28.** Yellow solid (purified by column chromatography, silica gel, $CH_2Cl_2$). Yield: 44%. Mp: 267 °C (from DSC). Purity (HPLC), 99+%. $^1$H NMR ($d_8$-THF, 500 MHz): δ (ppm) = 6.58 (d, $^2J$ = 58.5 Hz, 2H, -CHF), 4.28 (t, $J$ = 7 Hz, 4H), 4.19 (t, $J$ = 6.5 Hz, 4H), 2.15 (m, 4H). $^{13}$C NMR ($d_8$-THF, 500 MHz): δ (ppm) = 160.9, 135.2, 128.1, 127.1, 121.2-105.6 (-$CF_2$-), 100.9–98.3 (-CHF-), 63.9, 39.9, 28.5. MALDI-TOF MS calc. for $[C_{30}H_{14}Br_4F_{20}N_2NaO_8]^+$: 1248.71; found m/z: 1251.60 $[M+Na]^+$.

**29.** Yellow solid (purified by column chromatography, silica gel, $CH_2Cl_2$/hexanes, 2:1). Yield: 48%. Mp: 123 °C (from DSC). Purity (HPLC), 99+%. $^1$H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 7.61 (s, 4H), 6.05 (d, $^2J$ = 53.5 Hz, 6H, -CHF), 5.39 (s, 4H). $^{13}$C NMR ($CDCl_3$, 500 MHz): δ (ppm) = 160.0, 143.5, 136.7, 136.5, 133.3, 127.0, 125.7, 122.3, 121.0-104.5 (-$CF_2$-), 99.2–96.6 (-CHF-), 44.8. MALDI-TOF MS calc. for $[C_{58}H_{14}Br_4F_{60}N_2O_{16}]^+$: 2449.61; found m/z: 2452.34 $[M]^+$.

**30.** Yellow solid (purified by column chromatography, silica gel, $CH_2Cl_2$/hexanes, 2:1). Yield: 47%. Mp: 116 °C (from DSC). Purity (HPLC), 99+%. $^1$H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 7.29 (s, 4H), 6.05 (d, $^2J$ = 53.5 Hz, 6H, -CHF), 4.48 (t, $J$ = 7.8 Hz, 4H), 3.13 (t, $J$ = 7.5 Hz, 4H). $^{13}$C NMR ($CDCl_3$, 500 MHz): δ (ppm) = 159.8, 143.4, 138.9, 136.2, 132.2, 126.9, 125.5, 121.5, 120.9-104.4 (-$CF_2$-), 99.1–96.5 (-CHF-), 43.1, 33.8. MALDI-TOF MS calc. for $[C_{60}H_{18}Br_4F_{60}N_2O_{16}]^+$: 2477.64; found m/z: 2482.16 $[M]^+$.

**31.** Yellow solid (purified by column chromatography, silica gel, $CH_2Cl_2$/hexanes, 2:1). Yield: 37%. Mp: 130 °C (from DSC). Purity (HPLC), 99+%. $^1$H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 7.21 (s, 4H), 6.04 (d, $^2J$ = 53 Hz, 6H, -CHF), 4.31 (t, $J$ = 7.3 Hz, 4H), 2.82 (t, $J$ = 8 Hz, 4H), 2.14 (m, 4H). $^{13}$C NMR ($CDCl_3$, 500 MHz): δ (ppm) = 159.9, 143.3, 142.1, 136.11, 136.06, 131.3, 126.9, 125.6, 120.6-104.4 (-$CF_2$-), 99.1–96.5 (-CHF-), 42.3, 33.1, 28.7. MALDI-TOF MS calc. for $[C_{62}H_{22}Br_4F_{60}N_2O_{16}]^+$: 2505.67; found m/z: 2506.19 $[M]^+$.




**Sodium 1,1-dicyanoethylene-2,2-dithiolate (33).** This compound was synthesized according to a literature procedure.[S3]

**General Procedure for the Synthesis of Naphthalene Bisimides fused with 2-(1,3-dithiol-2-ylidene)malonitrile groups.** A solution of tetrabromonaphthalene diimide derivative (1 eq.) and sodium 1,1-dicyanoethylene-2,2-dithiolate **33** (3 eq.) in dry THF was stirred at 50 °C under nitrogen atmosphere for 1 h. The mixture was cooled to room temperature and the solvent removed *in vacuo*. The crude product was purified by column chromatography.

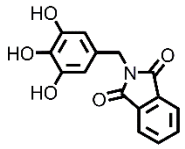
**34.** Red solid (purified by column chromatography, silica gel, EtOAc/$CH_2Cl_2$, 1:50). Yield: 41%. Mp > 350 °C. Purity (HPLC), 99+%. $^1$H NMR ($d_8$-THF, 500 MHz): δ (ppm) = 6.64 (d, $^2J$ = 52 Hz, 2H, -C*H*F), 4.41 (t, $J$ = 7 Hz, 4H, NC$H_2$), 4.24 (t, $J$ = 6.3 Hz, 4H, -C$H_2$O-), 2.23 (m, 4H, NCH$_2$C$H_2$CH$_2$O). $^{13}$C NMR ($d_8$-THF, 500 MHz): δ (ppm) = 183.4 (=$CS_2$), 163.4 (C=O), 144.9, 126.4, 117.9, 112.7 (C≡N), 121.7-105.3 (-$CF_2$-), 100.9–98.3 (-CHF-), 71.4 (=C(CN)$_2$), 63.7, 39.6, 28.3. MALDI-TOF MS calc. for $[C_{38}H_{14}AgF_{20}N_6O_8S_4]^+$: 1296.85; found m/z: 1297.24 $[M+]^+$.

**35.** Brown solid (purified by column chromatography, silica gel, EtOAc/hexanes, 2:3). Yield: 42%. Mp: 296 °C (from DSC). Purity (HPLC), 99+%. $^1$H NMR ($d_8$-THF, 500 MHz): δ (ppm) = 7.84 (s, 4H, Ar*H*), 6.78 (d, $^2J$ = 52 Hz, 6H, -C*H*F), 5.52 (s, 4H, NC$H_2$). $^{13}$C NMR ($d_8$-THF, 500 MHz): δ (ppm) = 182.8

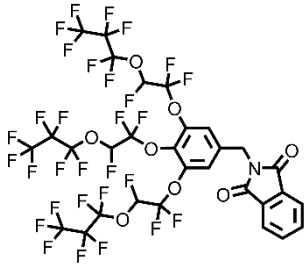
(=$CS_2$), 163.6 (C=O), 145.3, 144.1, 138.0, 134.3, 126.3, 124.2, 119.6, 112.6 (C≡N), 121.6-105.5 (-$CF_2$-), 100.6–98.1 (-CHF-), 71.7 (=$C(CN)_2$), 44.9. MALDI-TOF MS calc. for $[C_{66}H_{14}AgF_{60}N_6O_{16}S_4]^+$: 2520.74; found m/z: 2520.59 $[M+Ag]^+$.

**36.** Red solid (purified by column chromatography, silica gel, EtOAc/hexanes, 2:3). Yield: 47%. Mp: 268 °C (from DSC). Purity (HPLC), 99+%. $^1$H NMR ($d_8$-THF, 500 MHz): δ (ppm) = 7.59 (s, 4H, Ar*H*), 6.78 (d, $^2J$ = 51.5 Hz, 6H, -C*H*F), 4.53 (t, *J* = 8 Hz, 4H, NC$H_2$), 3.22 (t, *J* = 8 Hz, 4H, $NCH_2CH_2$). $^{13}$C NMR (*d*-THF, 500 MHz): δ (ppm) = 183.2 (=$CS_2$), 163.3 (C=O), 145.0, 144.3, 140.8, 133.2, 126.3, 122.9, 121.7, 112.7 (C≡N), 120.4-105.5 (-$CF_2$-), 100.7–98.1 (-CHF-), 71.5 (=$C(CN)_2$), 43.2, 34.1. MALDI-TOF MS calc. for $[C_{68}H_{18}F_{60}N_6NaO_{16}S_4]^+$: 2464.86; found m/z: 2464.85 $[M+Na]^+$.

**37.** Brown solid (purified by column chromatography, silica gel, EtOAc/hexanes, 2:3). Yield: 39%. Mp: 296 °C (from DSC). Purity (HPLC), 99+%. $^1$H NMR ($d_8$-THF, 500 MHz): δ (ppm) = 7.45 (s, 4H, Ar*H*), 6.72 (d, $^2J$ = 52 Hz, 6H, -C*H*F), 4.38 (t, *J* = 7 Hz, 4H, NC$H_2$), 2.94 (t, *J* = 8 Hz, 4H, $NCH_2CH_2CH_2$), 2.18 (m, 4H, $NCH_2CH_2CH_2$). $^{13}$C NMR ($d_8$-THF, 500 MHz): δ (ppm) = 183.4 (=$CS_2$), 163.4 (C=O), 144.9, 144.1, 132.2, 126.2, 121.8, 121.7, 119.6, 112.6 (C≡N), 120.4-105.5 (-$CF_2$-), 100.6–98.0 (-CHF-), 71.3 (=$C(CN)_2$), 42.1, 33.5, 29.9. MALDI-TOF MS calc. for $[C_{70}H_{22}AgF_{60}N_6O_{16}S_4]^+$: 2576.81; found m/z: 2577.20 $[M+Ag]^+$.



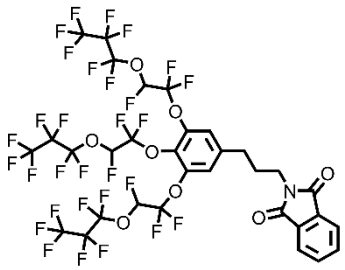
**2-(3,4,5-Trihydroxybenzyl)isoindoline-1,3-dione (38).** This compound was synthesized according to a literature procedure.[S4]



**2-(3,4,5-Tris(1,1,2-trifluoro-2-(perfluoropropoxy)ethoxy)benzyl)isoindoline-1,3-dione (39).**

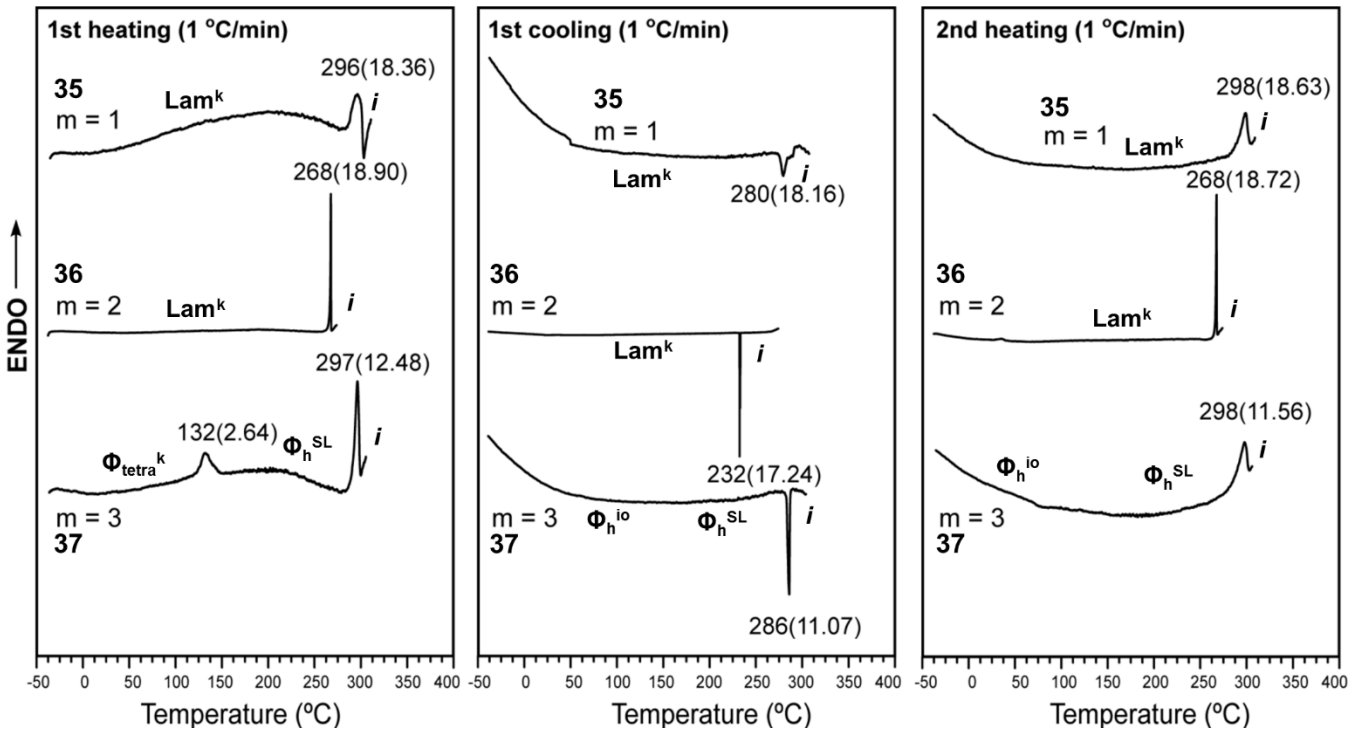
Perfluoropropyl vinyl ether (10.1 g, 37.9 mmol) was added to a sealed (with septum) round-bottomed flask (magnetic stirrer bar) under $N_2$ atmosphere at 0 °C. The flask was maintained at 0 °C while a solution of compound **38** (3.00 g, 10.5 mmol) in dry DMF (50 mL) was added. Potassium *tert*-butoxide (0.35 g, 3.2 mmol) was subsequently added to the reaction mixture. The temperature was maintained at

0 °C for 2 h. The reaction mixture was allowed to warm to room temperature whereupon it was stirred for 48 h. The solution was poured into ice-cold water (300 mL) containing concentrated hydrochloric acid (3 mL) and extracted with ethyl acetate. The combined organics were washed with water, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residual oil was purified by dry column vacuum chromatography[S6] (silica gel, hexane → 25% ethyl acetate in hexane) to give the product as a colorless oil (6.85 g, 60%). Purity (HPLC), 99+%. $^1$H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 7.91–7.84 (m, 2H), 7.78–7.71 (m, 2H), 7.44 (s, 2H), 6.05 (d, $^2J$ = 52.2 Hz, 3H, -CHF), 4.85 (s, 2H).



**2-(3-(3,4,5-Tris(1,1,2-trifluoro-2-(perfluoropropoxy)ethoxy)phenyl)propyl)isoindoline-1,3-dione (40).** A flask was charged with compound **23** (0.35 g, 0.34 mmol) and potassium phthalimide (75 mg, 0.40 mmol), evacuated and filled with $N_2$. Dry DMF (3 mL) was added *via* syringe. The mixture was heated to 100 °C whereupon it was fitted with a Drierite drying tube and stirred for 12 h. The mixture was allowed to cool to room temperature and poured into cold water (30 mL). The mixture was extracted with ethyl acetate (20 mL × 3), and the combined organics were washed with water (50 mL) and brine (50 mL), dried ($MgSO_4$) and filtered. The solvent was fully evaporated to produce the desired phthalimide which was used in the next step without further purification (0.30 g, 81%). $^1$H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 7.75–7.73 (m, 2H), 7.65–7.62 (m, 2H), 7.11 (s, 2H), 6.07 (d, $^2J$ = 53.3 Hz, 3H, -CHF), 3.69 (t, $J$ = 6.9 Hz, 2H), 2.66 (t, $J$ = 7.6 Hz, 2H), 1.97 (m, 2H).

## 4. Supporting DSC Measurements

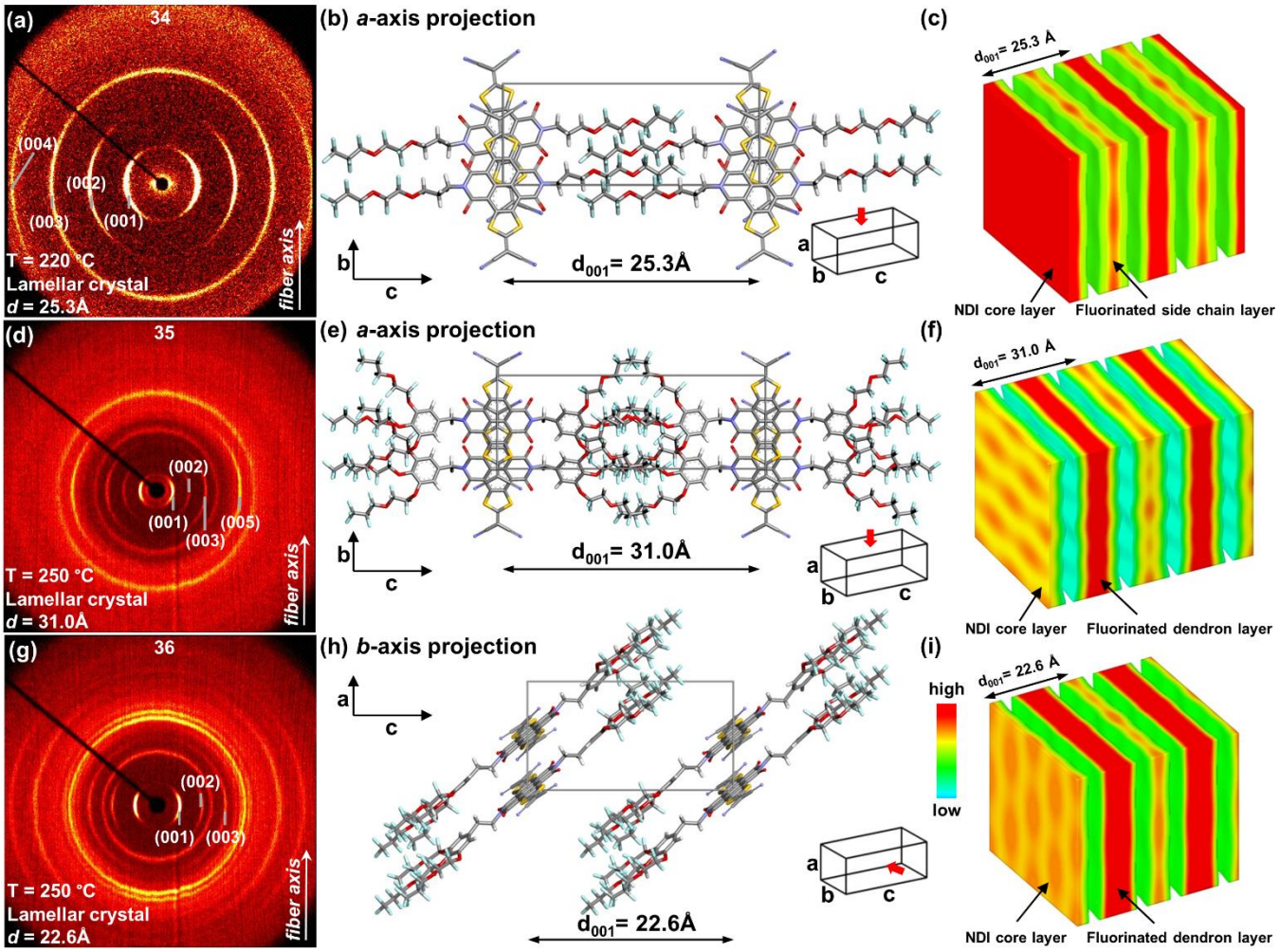



**Supporting Figure SF1**. DSC traces of **35**, **36** and **37** recorded with heating and cooling rates of 1 °C/min. Phases, transition temperatures, and associated enthalpy changes (in brackets in kcal/mol) are indicated. Phase notation: $\mathbf{Lam^k}$ – lamellar crystalline phase; $\mathbf{\Phi_{tetra}^k}$ – columnar tetragonal crystalline phase; $\mathbf{\Phi_h^{io}}$ – 2D hexagonal phase with intracolumnar order; $\mathbf{\Phi_h^{SL}}$ – 2D hexagonal superlattice.

## 5. Structural Analysis of 34, 35, and 36 (*m* = 1, 2, 3) based on XRD Fiber Patterns and Reconstructed Electron Density Maps.

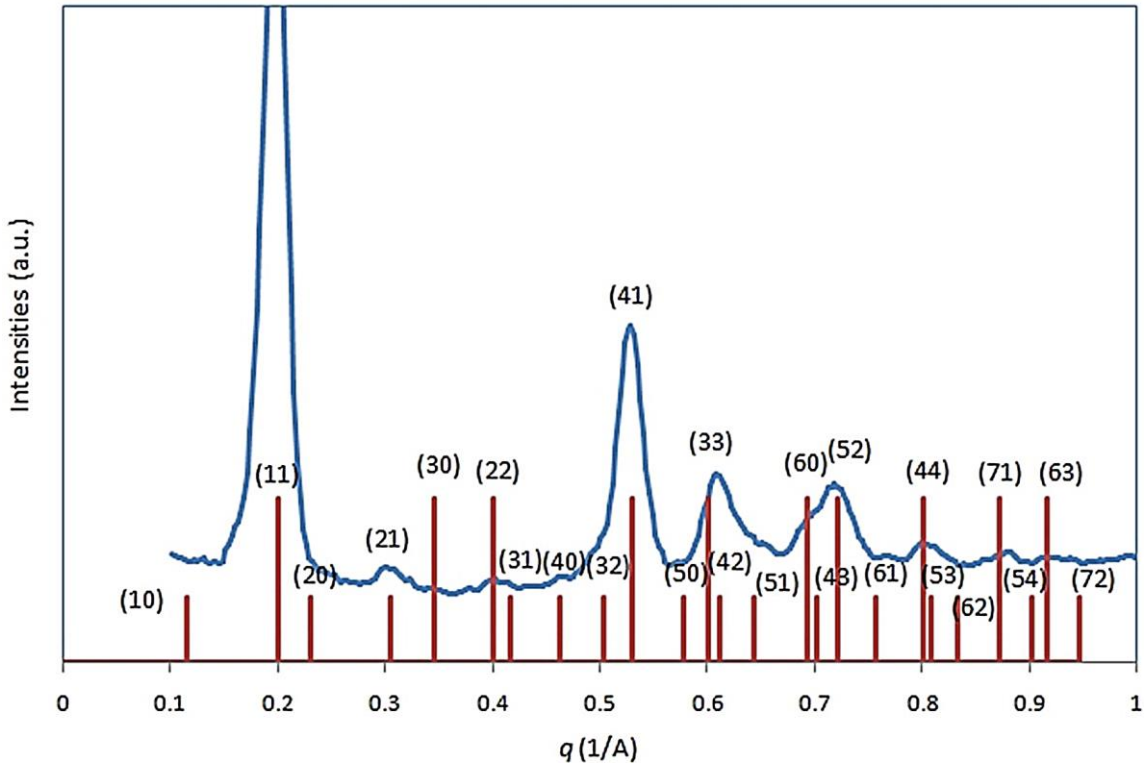
Sharp equatorial reflections were observed in all XRD patterns collected from the oriented fibers of **34** (Supporting Figure SF2a) and of dendronized NBI derivatives **35** (*m* = 1) (Supporting Figure SF2d) and **36** (*m* = 2) (Supporting Figure SF2g), indicating the formation of lamellar crystals with well-defined layer spacing. The crystal *c*-axis was defined as parallel to the layer normal and perpendicular to the fiber axis. The layer thickness ($d_{001}$) of the lamellar crystals were determined according to the *d*-spacing of equatorial reflections. As shown in the projections of molecular models (Supporting Figure SF2b, e, h), the layer thickness of crystalline **34** is 25.3 Å, that of **35** with *m* = 1 is 31.0 Å and that of **36** with *m* = 2 is 22.6 Å. The side chains in **34** are interdigitated in order to achieve effective space filling, while in

**35** the dendronized side chains exhibit less interdigitation and therefore **35** self-assembles to form lamellar crystals with a larger layer thickness. In the case of **36**, the observed layer thickness is even smaller than for **34**, indicating a tilted molecular arrangement with respect to the *c*-axis (lamellar normal). The relative electron distribution within the unit cell was reconstructed according to experimental XRD patterns and based on a face-centered orthorhombic lattice. Two repeat units along the *c*-axis are shown in Supporting Figure SF2c, f, i.




**Supporting Figure SF2**. X-ray diffraction patterns of lamellar crystals collected from the oriented fibers of (a) linear **34**, (d) **35**, and (f) **36** at indicated temperatures. Fiber axis, temperature, phase, and *d*-spacings are indicated. (b, e, h) The corresponding 2D projection of lattice models. Red arrows indicate axis of projection. (c, f, i) Reconstructed relative electron density distributions showing the lamellar *d*-spacing.

## 6. Supporting XRD Analysis




**Supporting Figure SF3**. Diffraction pattern of **37** (radial scan) at 250 ºC, $a$ = 62.8 Å. The expected diffraction peak positions are marked by red lines (those belonging to the simple hexagonal lattice are shown with longer red lines, whereas those belonging only to the superlattice are shown with shorter red lines). In addition to the (21) peak, (32), (42) and (51) peaks of the superlattice can also be identified.

## 7. Reconstruction of Electron Density Maps and Selection of Phase Combinations

In X-ray crystallography, a 3D periodic crystalline structure is represented by its corresponding electron density distribution $\rho(x,y,z)$, where $x$, $y$, $z$ are the fractional coordinates of a point in the unit cell along the $a$, $b$ and $c$ cell axes, respectively. The 3D periodic electron density $\rho(x,y,z)$ can be written as a Fourier series:

$$\rho(x,y,z) = \sum_{hkl} F_{hkl} \exp[i2\pi(hx + ky + lz)] \qquad (1)$$

In equation (1), the structure factor $F_{hkl}$ is a complex number, $h$, $k$, and $l$ are integers and the combination [$hkl$] describes a set of Miller planes in the crystal structure from which a diffraction peak with indices ($hkl$) is generated by the constructive interference of reflected X-rays. The structure factor $F_{hkl}$ is related to the observed diffraction intensity $I_{hkl}$ thus:

$$I_{hkl} \propto |F_{hkl}|^2 \qquad (2)$$

When only a relative electron density fluctuation is of interest, as in this paper, we can simply write the relative electron density as

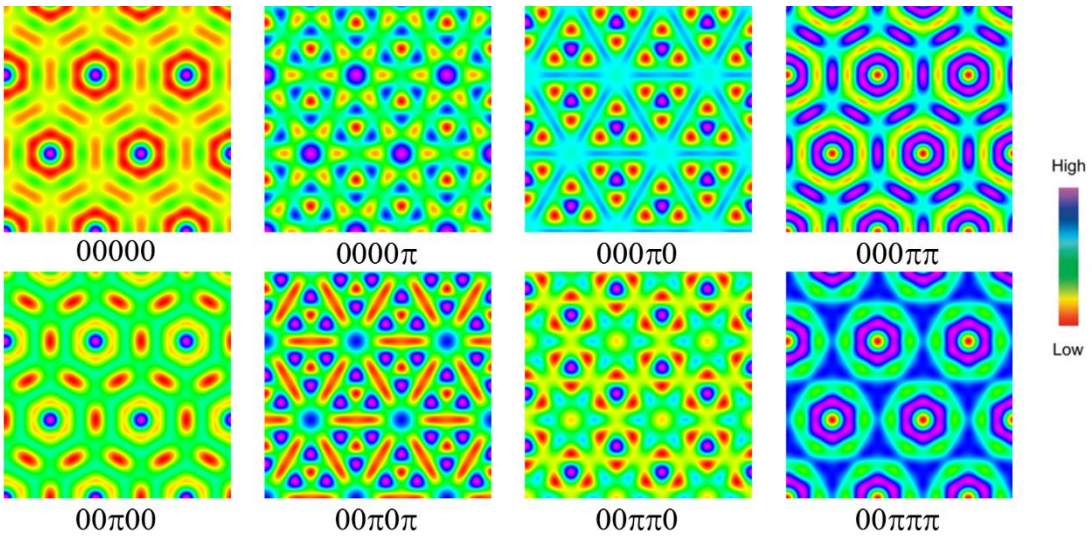
$$\rho(x,y,z) = \sum_{hkl} \sqrt{I_{hkl}} \exp[i2\pi(hx + ky + lz) + i\phi_{hkl}] \quad (3)$$

Unfortunately, the phase angle $\phi_{hkl}$ of the structure factor $F_{hkl}$ cannot be determined from X-ray diffraction data. For a centrosymmetric structure, however, the structure factor $F_{hkl}$ is always a real number. Consequently $\phi_{hkl}$ can only have values of 0 or π. Moreover, mesophases normally exhibit only a limited number of diffraction peaks due to their intrinsic local disorder and large thermal fluctuations. In such cases, it is possible to reconstruct electron density maps of all possible phase combinations, and to decide the best candidate map(s) on their physical merits afterwards. Knowledge about the chemical formulae of the compounds, the sizes of and the distances between different parts of the molecules and other physical information of the sample such as density is combined with the reconstructed candidate maps, in order to select the best phase combination(s).

**Supporting Table ST1.** The observed diffraction peaks of the low temperature $\mathbf{\Phi_h^{io}}$ phase of **37**, their *d*-spacings (experimental and calculated), intensities, multiplicities and phases. The intensities are obtained from fiber diffraction and corrected for multiplicity and the diffraction geometry. For easier comparison to the high temperature phase, the intensities are normalized to that of the (21) diffraction peak (or the (41) peak of the $\mathbf{\Phi_h^{SL}}$ superlattice phase).

| (*hk*) | $d_{hk}$ (exp.) | $d_{hk}$ (calc.) $a$ = 34.3 Å | Intensities | Multiplicity | Phase |
|---|---|---|---|---|---|
| (10) | 30.4 | 29.8 | 6.9 | 6 | 0 |
| (11) | 17.1 | 17.2 | 23.3 | 6 | 0 |
| (20) | 15.0 | 14.9 | 32.1 | 6 | π |
| (21) | 11.3 | 11.3 | 100.0 | 12 | π |
| (30) | 9.86 | 9.92 | 103.8 | 6 | π |
| (22) | 8.60 | 8.60 | 84.0 | 6 | 0 |
| (31) | 8.29 | 8.26 | 60.0 | 12 | 0 |

**Low temperature $\mathbf{\Phi_h^{io}}$ phase of 37.** Using equation (3), and the intensities as given in Supporting Table ST1, electron density maps of different phase combinations were reconstructed and compared. For illustrative purposes, relatively low resolution reconstructed maps using only the first five diffraction peaks are shown in Supporting Figure SF4.



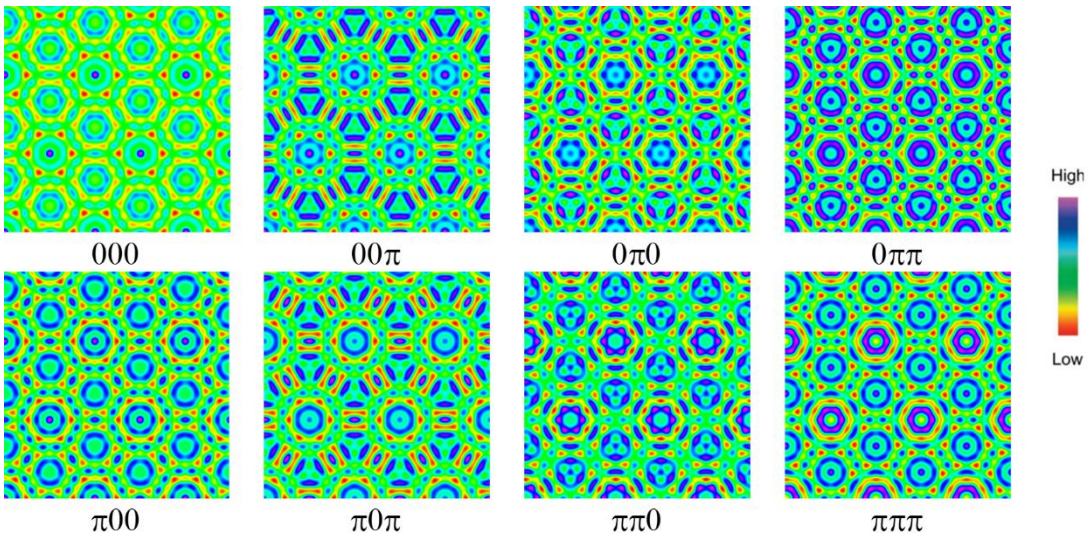

**Supporting Figure SF4**. Reconstructed electron density maps of the low temperature $\Phi_h^{io}$ phase, using the first five observed reflections.

In mesophases it is expected that different chemical moieties will separate from each other into different regions, and that the interface between such regions will be minimized. Accordingly, visual inspection of the eight maps in Supporting Figure SF4 would easily point to phase combinations (00000), (000ππ), (00π00) and (00πππ) to be better choices than the other four. Further consideration of the molecules themselves, namely that the NBI core and fluorinated end chains should have high electron density while the spacer and other parts should have low electron density, would favor the two maps (000ππ) and (00πππ). Upon the addition of the remaining two peaks, (22) and (31), the best map is chosen as shown in Figure 4a of the manuscript.

**Supporting Table ST2.** The observed diffraction peaks of the high temperature $\Phi_h^{SL}$ phase of **37**, their *d*-spacings (experimental and calculated), intensities, multiplicities and phases. The intensities are obtained from fiber diffraction and corrected for multiplicity and the diffraction geometry. The intensities are normalized to that of the (41) diffraction peak. For easy comparison to low temperature phase the indices of corresponding peaks in the $\Phi_h^{io}$ phase are also listed.

| (*hk*) $\Phi_h^{SL}$ | (*hk*) $\Phi_h^{io}$ | $d_{hk}$ (exp.) | $d_{hk}$ (calc.) $a$ = 34.3 Å | Intensities | Multiplicity | Phase |
|---|---|---|---|---|---|---|
| (11) | (10) | 31.7 | 31.4 | 86.9 | 6 | 0 |
| (22) | (20) | 15.7 | 15.7 | 5.4 | 6 | π |
| (41) | (21) | 11.9 | 11.9 | 100.0 | 12 | π |
| (33) | (30) | 10.5 | 10.4 | 17.4 | 6 | π |
| (60) | (22) | 9.07 | 9.06 | 41.7 | 6 | 0 |
| (52) | (31) | 8.73 | 8.60 | 52.7 | 12 | 0 |
| (21) | - | 20.6 | 20.6 | 2.7 | 12 | 0 |
| (32) | - | 12.5 | 12.5 | 8.0 | 12 | 0 |
| (42) | - | 10.3 | 10.3 | 39.6 | 12 | π |
| (51) | - | 9.80 | 9.77 | 10.0 | 12 | π |

**High temperature $\Phi_h^{SL}$ phase of 37.** The selection of phase combination for the high temperature phase is simplified with the assumption that its average structure should be similar to that of the low temperature $\Phi_h^{io}$ phase. The intensities of most $\Phi_h^{io}$ peaks do not change very much upon phase transition, and while the intensity of the (10) peak does change, it does so continuously with increasing temperature. Therefore we have adopted the same phase combinations for those peaks as was used for the low temperature $\Phi_h^{io}$ phase. This simplified the consideration of all possible phase combinations to give just 16 remaining phase combinations arising from the pure superlattice peaks. Eight of the maps are shown in Supporting Figure SF5. The best phase combination (0ππ) was chosen to be that combination which produced a map most similar to, or with least distortion of, that of the low temperature $\Phi_h^{io}$ phase.




**Supporting Figure SF5**. Reconstructed electron density maps of the high temperature $\mathbf{\Phi_h^{SL}}$ phase, using all ten reflections as listed in Supporting Table ST2. The listed phases correspond to the last three reflections.

## 8. References for the Supporting Information

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