Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Self-Assembly of Semifluorinated Janus-Dendritic Benzamides into Bilayered Pyramidal Columns

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Experimental Section

Materials. Methyl 3,4,5-trihydroxybenzoate (98%), methyl 4-hydroxybenzoate (99%), 1-bromododecane (98%), 1,2,3-trihydroxybenzene (99%), hydrazine monohydrate (98%), α,α,α-trifluorotoluene (99%) (all from Acros), heptadecafluoro-1-iodooctane (98%) (Fluka), 1,2,3-trimethoxybenzene (98%), 1,2-benzenediol (catechol, 99%), 1,1,2-trichlorotrifluoroethane (Freon® 113), graphite powder (1-2 micron), aluminum oxide (activated, basic, Brockmann I, standard grade, ~150 mesh, 58 Å) (all from Aldrich), DMF, MeOH, EtOH, $MgSO_4$, H_2SO_4, acetone, diethyl ether, ethyl acetate (all from Fisher, ACS reagents), silica gel (Sorbent Technology) were used as received. Hexane (ACS reagent grade, Fisher Scientific) was washed with H_2SO_4 (three times), saturated $NaHCO_3$, and water and dried over $CaCl_2$. Dichloromethane (Fisher, ACS reagent grade) was refluxed over CaH_2 and freshly distilled before use. THF (Fisher, ACS reagent grade) was refluxed over sodium/benzophenone until the solution turned purple and distilled before use. All other chemicals were commercially available and were used as received.

Techniques. ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz) and ^{19}F NMR (470 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) on silica gel coated aluminum plates (with F_{254} indicator; layer thickness, 200 μm; particle size, 2-25 μm; pore size 60Å, SIGMA-Aldrich) and high pressure liquid chromatography (HPLC) using a Perkin-Elmer Series 10 high pressure liquid chromatograph equipped with a LC-100 column oven, Nelson Analytical 900 Series integrator data station and two Perkin-Elmer PL gel columns of 5 X 10^2 and 1 X 10^4 Å, THF was used as solvent at the oven temperature of 40 °C. Detection was by UV absorbance at 254 nm. Melting points were

measured using a uni-melt capillary melting point apparatus (Arthur H. Thomas Company) and were uncorrected.

Thermal transitions were measured on a TA Instrument 2920 modulated differential scanning calorimeter (DSC). In all cases, the heating and the cooling rates were 10 °C min^{-1}. The transition temperatures were measured as the maxima and minima of their endothermic and exothermic peaks. Indium was used as calibration standard. An Olympus BX-51 optical polarized microscope (100 X magnification) equipped with a Mettler FP 82HT hot stage and a Mettler Toledo FP90 central processor was used to verify thermal transitions and characterize anisotropic textures. Density (ρ) measurements were carried out by floatation in gradient columns at 20 °C.

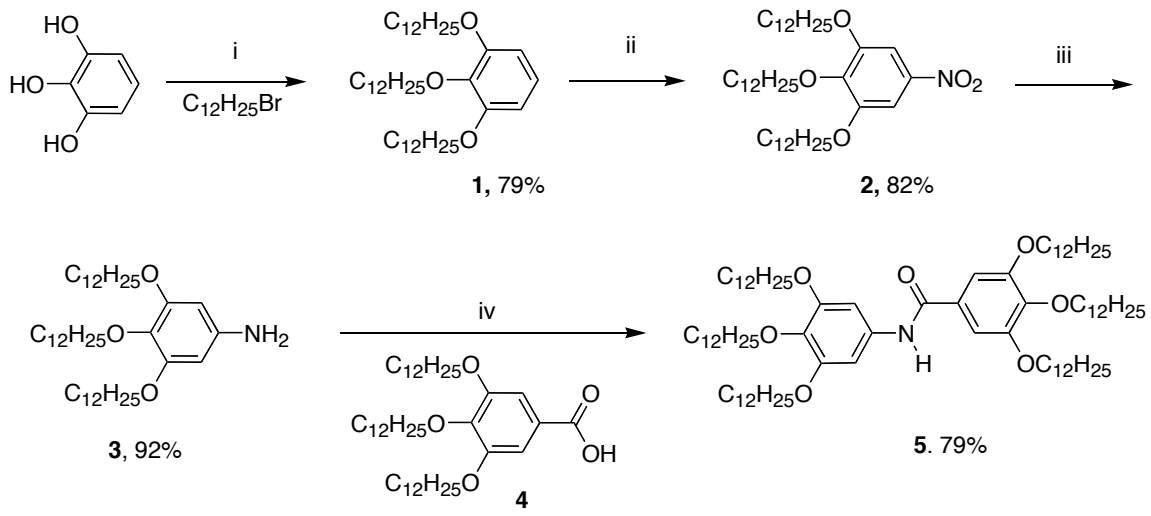
X-ray diffraction measurements were carried out with Cu-K_α radiation from a Bruker-Nonius FR-591 rotating anode x-ray source with a 0.2 x 2.0 mm^2 filament operated at 3.4 kW. The beam was collimated and focused by a single bent mirror and sagitally focusing Ge (111) monochromator, resulting in a 0.2 X 0.2 mm^2 spot on a multi wire detector 125 cm from the sample. To minimize attenuation and background scattering, an integral vacuum was maintained along the length of the flight tube and within the sample chamber. The samples were held in a temperature controlled (± 0.1 °C) oven. Aligned samples for fiber XRD experiments were prepared using a custom made extrusion device. The powdered sample (~ 10 mg) was heated inside the extrusion device to isotropic transition temperature. After cooling slowly from isotropic, the fiber was extruded in the mesophases and cooled to room temperature. Typically the aligned samples have a thickness of ~ 0.3-0.7 mm and a length of ~ 3-7 mm. All X-ray diffraction measurements were done with the aligned sample axis perpendicular to the beam direction.

Molecular modeling calculations were done using the Materials Studio Modeling version 3.1 software from Accelrys. The package Discover module was used to perform the energy minimizations on the supramolecular structures with the following settings: PCFF or COMPASS force fields and Fletcher-Reeves algorithm for the conjugate gradient method.

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry was carried out on a PerSeptive Biosystems-Voyager-DE (Framingham, MA) mass spectrometer operating in linear mode. The spectrometer equipped with a nitrogen laser (337 nm) was calibrated using Angiotensin II and Bombesin as standards. The laser steps and voltages applied were adjusted as a function of the molecular weight and the nature of the compound. The matrix used in MALDI-TOF mass spectrometry was 3,5-dimethoxy-4-hydroxy-*trans*-cinnamic acid. The solvent used for both matrix and sample was tetrahydrofuran (THF). A typical procedure used for sample preparation was as follows. The matrix (10 mg) was dissolved in 1 mL of THF. The sample concentration was 5-10 mg/ mL. The matrix solution (25 μL) and the sample solution (5 μL) were mixed well, and then 0.5 μL of the resulting solution was loaded into the MALDI-plate and dried before inserting into the vacuum chamber of the MALDI machine.

Synthesis. The nitrating agent (20% HNO_3 on silica gel by titration with 1N NaOH using phenolphthalein as an indicator) was prepared according to a literature procedure[1] and was used after drying in air for several days. 4-*N,N*-Dimethylaminopyridinium *p*-toluenesulfonate (DPTS),[2] and 2-chloro-4,6-dimethoxy-1,3,5-triazine (CDMT)[3] were prepared according to literature procedures. The synthesis of 12-bromo-

1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro dodecane has been reported previously.[4]



Reagents and conditions: i) K_2CO_3, DMF, 60 °C, 4 h; ii) CH_2Cl_2, $SiO_2 \cdot HNO_3$, 25 °C, 15 min; iii) $NH_2NH_2 \cdot H_2O$, graphite, EtOH, reflux, 24 h; iv) DCC, DPTS, CH_2Cl_2, 25 °C, 16 h.

Scheme 1 (supporting). Synthesis of (3,4,5)12G1-(3,4,5)12G1-benzamide (**5**)

1,2,3-Tris-dodecyloxybenzene (1). A 500 mL three-neck round bottom flask, equipped with a teflon-coated magnetic stir bar and an Ar inlet-outlet, was charged with 1,2,3-trihydroxybenzene (12.6 g, 0.10 mole), K_2CO_3 (69.1 g, 0.50 mole) and DMF (160 mL) and degassed for 1 h. To the reaction mixture 1-bromododecane (74.78 g, 0.30 mole) was added under Ar at 60 °C in small portions over 10 min. After 4 h at 60 °C, the reaction mixture was poured into stirring ice/water (1L). The creamy, granular solid was filtered and washed with H_2O. Two recrystallizations from isopropanol yielded 50.0 g (79.2%) of white solid. Purity (HPLC), 99+%; m.p. 38 – 39.5 °C (ref. [5]): 39-40 °C); TLC (EtOAc/hexane = 1/9): R_f = 0.79; ^{1}H NMR (500 MHz, $CDCl_3$, 30 °C, TMS): δ = 0.88 (t,

9H, CH_3), 1.26-1.34 (overlapped peaks, broad, 48H, $CH_3(CH_2)_8$), 1.47 (m, 6H, $CH_2(CH_2)_2O$), 1.78 (m, 6H, CH_2CH_2O), 3.96 (overlapped t, 6H, CH_2O), 6.54 (d, 2H, 4,6 position, J = 8.3 Hz), 6.90 (t, 1H, 5 position, J = 8.3); ^{13}C NMR (125 MHz, $CDCl_3$, 30 °C, TMS): δ = 14.3 (CH_3), 22.9 (CH_3CH_2), 26.3 ($CH_2CH_2CH_2O$), 29.6 ($CH_3CH_2CH_2CH_2$), 29.7 ($CH_3CH_2CH_2CH_2(CH_2)_5$), 29.9 (CH_2CH_2O, 1,3 position), 30.6 (CH_2CH_2O, 2 position), 32.2 ($CH_3CH_2CH_2$), 69.4 (CH_2O, 1,3 position), 73.6 (CH_2O, 2 position), 107.2 (4,6 position), 123.3 (5 position), 138.5 (2 position), 153.7 (1,3 position).

1,2,3-Tris-dodecyloxy-5-nitrobenzene (2). To a stirred suspension of $SiO_2 \cdot HNO_3$ (78.75 g, 0.25 mole, 20% of HNO_3 on SiO_2) in CH_2Cl_2 (400 mL) was rapidly added 1,2,3-tris-dodecyloxy benzene (**1**) (31.6 g, 0.05 mole) dissolved in CH_2Cl_2 (100 mL). The resulting red solution was stirred at room temperature for 15 min, after which time SiO_2 was filtered and washed several times with CH_2Cl_2. The solvent was evaporated on a rotary evaporator and the resulting red oil was dissolved in hexane (50 mL). Upon addition of cold MeOH (500 mL) with vigorous shaking, the product separated as a yellow solid. The solid was filtered, washed with cold MeOH and dried. Recrystallization from isopropyl alcohol (active charcoal) yielded 27.8 g (82.2%) of white solid. Purity (HPLC): 99+%; m.p. 53 – 54 °C (ref [5]): 54.5 – 55.5 °C); TLC (EtOAc/hexane = 1/9): R_f = 0.73; ^1H NMR (500 MHz, $CDCl_3$, 30 °C, TMS): δ = 0.88 (t, 9H, CH_3), 1.26 (overlapped peaks, 48H, $CH_3(CH_2)_8$), 1.47 (m, 6H, $CH_2(CH_2)_2O$), 1.78 (m, 2H, CH_2CH_2O, *para* to NO_2), 1.83 (m, 4H, CH_2CH_2O, *meta* to NO_2), 4.04 (overlapped m, 6H, CH_2O, J = 6.7 Hz), 7.47 (s, 2H, ArH, *ortho* to $–NO_2$) ^{13}C NMR (125 MHz, $CDCl_3$, 30 °C, TMS): δ = 14.3 (CH_3), 22.9 (CH_3CH_2), 26.2 ($CH_2CH_2CH_2O$), 29.5 ($CH_3CH_2CH_2CH_2$), 29.7 ($CH_3CH_2CH_2CH_2(CH_2)_5$), 29.9 (CH_2CH_2O, 1,3 position), 30.5 (CH_2CH_2O, 2 position), 32.1 ($CH_3CH_2CH_2$), 69.7

(CH_2O, 1,3 position), 74.0 (CH_2O, 2 position), 102.4 (*ortho* to NO_2), 143.4 (*ipso* to NO_2), 144.1 (*para* to NO_2), 152.9 (*meta* to NO_2).

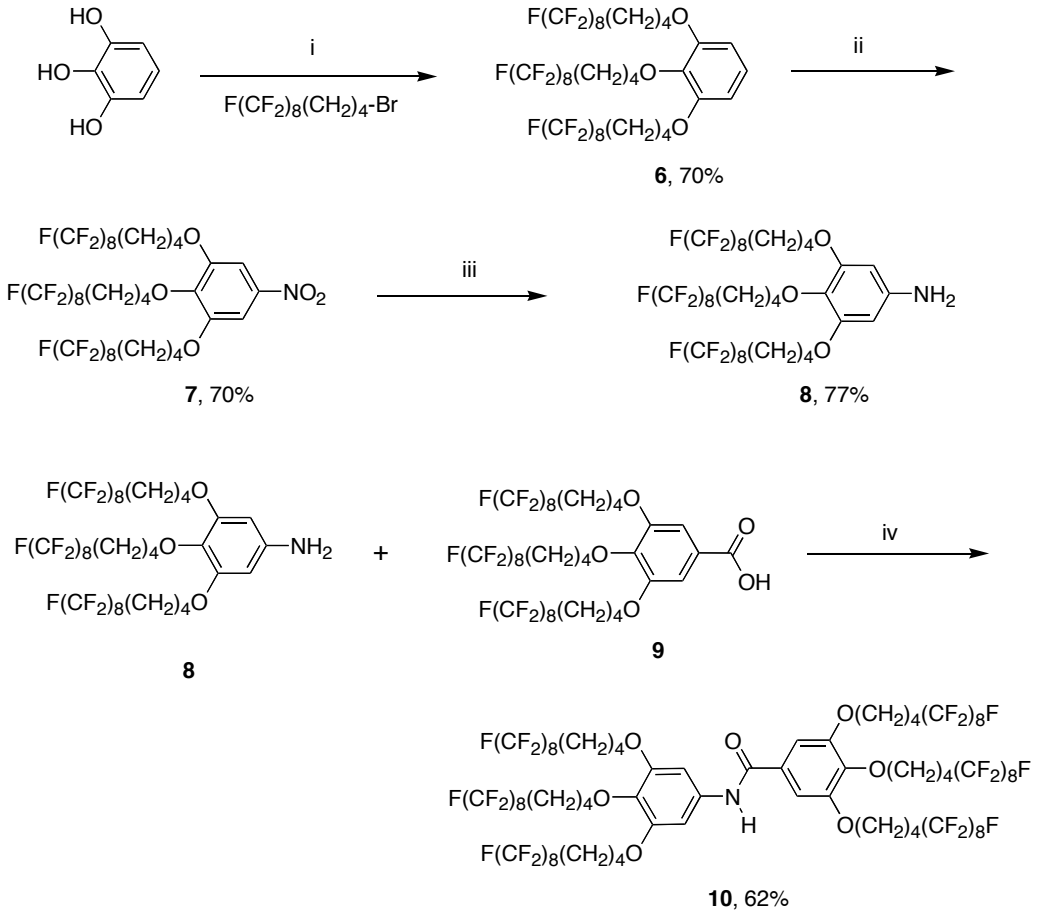
3,4,5-Tris-dodecyloxy-phenylamine (3). Compound **3** was synthesized by the reduction of **2** with hydrazine over graphite powder.[6] A mixture of compound **2** (21.37 g, 0.03 mole), $NH_2NH_2 \cdot H_2O$ (4.74 g, 0.09 mole) and graphite (15 g) in ethanol (200 mL) was refluxed under argon atmosphere for 24 h. The cooled mixture was diluted with CH_2Cl_2 (250 mL). Graphite was filtered washed several times with CH_2Cl_2. The colorless solution was concentrated on a rotary evaporator and the resulting white solid was dissolved in CH_2Cl_2 (150 mL). After precipitation in MeOH (1L), the obtained solid was collected by filtration and washed with cold MeOH. After drying under vacuum 18.9 g (92.7%) of a white powder was obtained. Purity (HPLC), 99+%; m.p. 67 – 68.5 °C (Ref. [5]): 71.5 – 72.5 °C); TLC (EtOAc/hexane = 1/9): R_f = 0.10; ^{1}H NMR (500 MHz, $CDCl_3$, 30 °C, TMS): δ = 0.88 (t, 9H, CH_3), 1.26 (overlapped peaks, 48H, $CH_3(CH_2)_8$), 1.46 (m, 6H, $CH_2(CH_2)_2O$), 1.75 (m, 6H, CH_2CH_2O), 3.46 (bs, 2H, NH_2), 3.84 (t, 2H, CH_2O, 4 position, J = 6.65 Hz), 3.91 (t, 4H, CH_2O, 3,5 positions, J = 6.55), 5.91 (s, 2H, ArH, *ortho* to NH_2); ^{13}C NMR (125 MHz, $CDCl_3$, 30 °C, TMS): δ = 14.5 (CH_3), 23.1 (CH_3CH_2), 26.5 ($CH_2CH_2CH_2O$), 29.8 ($CH_3CH_2CH_2CH_2$), 30.1 ($CH_3CH_2CH_2CH_2(CH_2)_5$), 30.2 (CH_2CH_2O, 3,5 position), 30.8 (CH_2CH_2O, 4 position), 32.4 ($CH_3CH_2CH_2$), 69.5 (CH_2O, 3,5 position), 74.0 (CH_2O, 4 position), 94.9 (*ortho* to NH_2), 131.6 (*para* to NH_2), 142.7 (*ipso* to NH_2), 154.1 (*meta* to NH_2).

3,4,5-Tris-dodecyloxy-benzoic acid (4). Compound **4** was synthesized according to the literature procedure.[5,7] After alkylation of methyl 3,4,5-trihydroxy benzoate (9.2 g, 0.05 mol) with 1-bromododecane (37.4 g, 0.15 mol) and anhydrous K_2CO_3 (34.6 g, 0.25 mol)

in DMF (125 mL), 28.2 g (82.0 %) of methyl 3,4,5-tris-dodecyloxy benzoate was obtained as a white solid. The ester (17.2 g, 25 mmol) was hydrolyzed with excess KOH (8,0 g, 125 mmol) in refluxing ethanol (95%, 125 mL). After refluxing for 2h, the reaction mixture was cooled to room temperature and the solution was acidified with dilute HCl to pH 1. The solution was poured into ice-cooled water (500 mL) and the precipitated solid was collected under vacuum filtration. Recrystallization from acetone yielded 15.5 g (92%) of white solid. Purity (HPLC), 99+%; m.p. 56 – 57.5 °C (ref. [5]): 60-61 °C); TLC (EtOAc/hexane = 1/9): R_f = 0.095; ^{1}H NMR (500 MHz, $CDCl_3$, 30 °C, TMS): δ = 0.88 (t, 9H, CH_3, *J* = 6.8), 1.26-1.33 (overlapped peaks, m, 48H, $CH_3(CH_2)_8$), 1.46 (m, 6H, $CH_2(CH_2)_2O$), 1.78 (m, 6H, CH_2CH_2O), 4.01 (overlapped t, 6H, CH_2O), 7.28 (s, 2H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$, 30 °C, TMS): δ = 14.3 (CH_3), 22.9 (CH_3CH_2), 26.3 ($CH_2CH_2CH_2O$), 29.6 – 30.6 ($CH_3CH_2CH_2(CH_2)_6$), 32.2 ($CH_3CH_2CH_2$), 69.4 (CH_2CH_2O,), 73.7 (CH_2O), 108.7 (*ortho* to CO_2H), 125.0 (*ipso* to CO_2H), 142.9 (*para* to CO_2H), 153.0 (*meta* to CO_2H), 171.6 ($PhCO_2H$).

3,4,5-Tris-dodecyloxy-*N*-(3,4,5-tris-dodecyloxy-phenyl)-benzamide (5). A 100 mL 3-neck round-bottom flask containing a teflon-coated magnetic stir bar was charged with compound **3** (2.6 g, 4.0 mmol), compound **4** (2.7 g, 4.0 mmol), DCC (1.65 g, 8.0 mmol), DPTS (120 mg, 0.4 mmol) and dry CH_2Cl_2 (40 mL). The mixture was stirred under argon for 24 h. The extent of the reaction was followed by TLC. After precipitation in methanol, the solids were collected by filtration and dried in air. Purification by column chromatography (EtOAc/Hexane, 1:9) produced 4.1 g (78.7 %) of **5** as a white solid. Purity (HPLC): 99%; thermal transitions and the corresponding enthalpy changes are summarized in Table 1. TLC (EtOAc/hexane = 1/9): R_f = 0.79; ^{1}H NMR (500 MHz,

$CDCl_3$, 30 °C, TMS): δ = 0.88 (t, 18H, CH_3, J = 6.8 Hz), 1.26 (overlapped m, 108H, $(CH_2)_9$), 1.46 (m, 12H, $CH_2CH_2CH_2OPh$), 1.79 (overlapped m, 12H, CH_2CH_2OPh), 3.98 (m, 12H, CH_2OPh), 6.90 (s, 2H, *ortho* to NHCO), 7.03 (s, 2H, *ortho* to CONH), 7.58 (s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$, 30^0C, TMS): δ = 14.3 (CH_3), 22.9 (CH_2CH_3), 26.3 ($CH_2CH_2CH_2OPh$), 29.6- 30.6 (CH_2CH_2OPh, $(CH_2)_6CH_2CH_2CH_3$), 32.2 ($CH_2CH_2CH_3$), 69.4, 69.8 (CH_2OPhNH), 73.7, 73.8 (CH_2OPhCO), 99.4 (*ortho* to NHCO), 106.0 (*ortho* to CONH), 130.1 (*ipso* to CONH), 133.8 (*para* to NHCO), 135.3 (*ipso* to NHCO), 141.8 ((*para* to CONH), 153.5 (*meta* to NHCO and CONH), 165.7 (CONH); MALDI-TOF *m*/*z*: 1303.98 (M^+, calculated 1303.16), 1326.25 ($[M+Na]^+$, calculated 1326.15), 1342.41 ($[M+K]^+$, calculated 1342.26).



Reagents and conditions: i) K_2CO_3, DMF, 70 °C, 6 h; ii) CH_2Cl_2, $SiO_2 \cdot HNO_3$, 25 °C, 12 h; iii) $NH_2NH_2 \cdot H_2O$, graphite, EtOH-THF, reflux, 24 h; iv) DCC, DPTS, α,α,α-trifluorotoluene, 50 °C, 4 h.

Scheme 2 (supporting). Synthesis of (3,4,5)12F8G1-(3,4,5)12F8G1-benzamide (**10**)

1,2,3-Tris-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heptadecafluoro-dodecyloxy) benzene (6). To a stirred solution of 1,2,3-trihydroxy benzene (440 mg, 3.5 mmol) and anhydrous K_2CO_3 (2.42 g, 17.5 mmol) in degassing DMF (35 mL), 12-bromo-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-dodecane (5.82 g, 10.5 mmol) was added at room temperature and stirred for 5 min. The temperature was raised to 70 °C and stirred for 6h under Ar. The reaction mixture was cooled to room temperature and partitioned between diethyl ether and water. After the aqueous phase was extracted with

diethyl ether, the combined organic phase was washed with dil. HCl and brine, dried over $MgSO_4$, concentrated, and evaporated in vacuo. Recrystallization from acetone yielded 3.8 g (70.3%) of **6** as a white crystal. Purity (HPLC): 99+%; m.p. 71 – 72.5 °C; TLC (EtOAc/hexane = 3/7): R_f = 0.74; ^{1}H NMR (500 MHz, $CDCl_3$, 30 °C, TMS): δ = 1.86 (m, 12H, $CF_2(CH_2)_2$), 2.15 (m, 6H, CH_2CH_2O), 3.97 (t, 2H, CH_2O, 2 position, *J* = 5.85 Hz), 4.02 (t, 4H, CH_2O, 1,3 position, *J* = 5.6), 6.56 (d, 2H, 4,6 position, *J* = 8.4), 6.95 (t, 1H, 5 position, *J* = 8.3); ^{19}F NMR (470 MHz, $CDCl_3$, 30 °C, TMS): δ = -81.5 (overlapped t, 9F, CF_3), -115.0 (m, 6F, CF_2CH_2), -122.4 (m, 18F, $(CF_2)_3CF_2CH_2$), -123.3 (s, 6F, $CF_3(CF_2)_2CF_2$), -124.1 (d, 6F, $CF_3CF_2CF_2$), -126.7 (d, 6F, CF_3CF_2); ^{13}C NMR (125 MHz, $CDCl_3$, 30 °C, TMS): δ = 17.3 ($CF_2CH_2CH_2$, 2 position), 17.4 ($CF_2CH_2CH_2$, 1,3 position), 28.9 (CH_2CH_2OAr, 1,3 position), 29.8 (CH_2CH_2OAr, 2 position), 30.6-30.9 (overlapped t, CF_2CH_2), 68.5 (CH_2OAr, 1,3 position), 72.6 (CH_2OAr, 2 position), 107.1 (4,6 position), 108.7-118.6 (m, CF_2), 123.7 (5 position), 138.3 (*ipso* to CH_2O, 2 position), 153.2 (*ipso* to CH_2O, 1,3 position).

1,2,3-Tris-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heptadecafluoro-dodecyloxy)-5-nitrobenzene (7). Compound **7** was synthesized by the same general procedure described for the synthesis of compound **2**. Over a stirred suspension of HNO_3 (3.3 g, 10 mmol, 20% of HNO_3 on SiO_2) in CH_2Cl_2 (30 mL) was added **6** (3.25 g, 2 mmol) in CH_2Cl_2-CFC-113 mixture (12 mL). The heterogeneous mixture was stirred overnight. Workup as **2** and recrystallization from acetone yielded 2.4 g (69.7%) of white crystals. Purity (HPLC): 99+%; m.p. 83 – 85 °C; TLC (EtOAc/hexane = 3/7): R_f = 0.77; ^{1}H NMR (500 MHz, $CDCl_3$, 30 °C, TMS): δ = 1.86 (m, 8H, $CF_2(CH_2)_2$, *meta* to NO_2), 1.94 (m, 4H, $CF_2(CH_2)_2$, *para* to NO_2), 2.2 (m, 6H, CH_2CH_2O), 4.1 (m, 6H, CH_2O), 7.5 (s, 2H, ArH); ^{19}F NMR

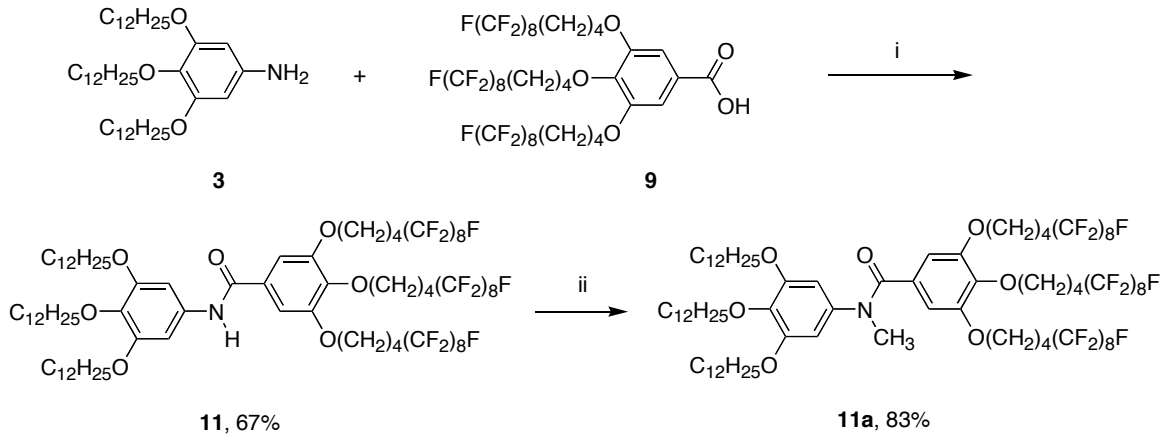
(470 MHz, $CDCl_3$, 30 °C, TMS): δ = -81.4 (overlapped t, 9F, CF_3), -114.8 (m, 6F, CF_2CH_2), -122.3 (m, 18F, $(CF_2)_3CF_2CH_2$), -123.1 (s, 6F, $CF_3(CF_2)_2CF_2$), -124.0 (d, 6F, $CF_3CF_2CF_2$), -126.5 (m, 6F, CF_3CF_2); ^{13}C NMR (125 MHz, $CDCl_3$, 30 °C, TMS): δ = 17.4 ($CF_2CH_2CH_2$, 4 position), 17.6 ($CF_2CH_2CH_2$, 3,5 position), 28.9 (CH_2CH_2OAr, 3,5 position), 29.9 (CH_2CH_2OAr, 4 position), 30.8-31.1 (overlapped t, CF_2CH_2), 69.2 (CH_2OAr, 3,5 position), 73.2 (CH_2OAr, 4 position), 102.8 (*ortho* to NO_2), 141.5 (*para* to NO_2), 143.8 (*ipso* to NO_2), 152.8 (*meta* to NO_2).

3,4,5-Tris-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heptadecafluoro-dodecyloxy)-phenyl amine (8). Compound **8** was synthesized by the same general procedure described for the synthesis of compound **3**. A solution containing **7** (1.7 g, 1.1 mmol) in THF (5 mL), $NH_2NH_2{\cdot}H_2O$ (163 mg, 3.3 mmol), graphite (1 g) and EtOH (25 mL) was refluxed for 24 h under argon atmosphere. After recrystallization from hexane-CH_2Cl_2 mixture (1/1) 1.3 g (76.9%) of pale yellow solid was obtained. Purity (HPLC): 99+%; m.p. 81-82 °C; TLC (EtOAc/hexane = 3/7): R_f = 0.12; ^{1}H NMR (500 MHz, $CDCl_3$, 30 °C, TMS): δ = 1.86 (m, 12H, $CF_2(CH_2)_2$,), 2.14 (m, 6H, CH_2CH_2O), 3.52 (s, 2H, NH_2), 3.85 (t, 2H, CH_2O, *para* to NH_2, *J* = 5.9 Hz), 3.95 (t, 4H, CH_2O, *meta* to NH_2), 5.91 (s, 2H, ArH); ^{19}F NMR (470 MHz, $CDCl_3$, 30 °C, TMS): δ = -81.5 (overlapped t, 9F, CF_3), -114.9 (m, 6F, CF_2CH_2), -122.2 (m, 18F, $(CF_2)_3CF_2CH_2$), -123.1 (s, 6F, $CF_3(CF_2)_2CF_2$), -124.1 (d, 6F, $CF_3CF_2CF_2$), -126.3 (m, 6F, CF_3CF_2); ^{13}C NMR (125 MHz, $CDCl_3$, 30 °C, TMS): δ = 17.5 ($CF_2CH_2CH_2$, 3,4,5 position), 29.0 (CH_2CH_2OAr, 3,5 position), 29.9 (CH_2CH_2OAr, 4 position), 30.6-31.0 (overlapped t, CF_2CH_2), 68.4 (CH_2OAr, 3,5 position), 73.0 (CH_2OAr, 4 position), 94.5 (*ortho* to NH_2), 111.2 (m, CF_2), 143.0 (*ipso* to NH_2), 153.6 (*meta* to NH_2).

3,4,5-Tris-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heptadecafluoro-dodecyloxy)-benzoic acid (9). Compound **9** was synthesized according to a literature procedure.[4] After alkylation of methyl 3,4,5-trihydroxy benzoate (0.92 g, 5 mmol) with 12-bromo-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-dodecane (8.32 g, 15 mmol) in the presence of anhydrous K_2CO_3 (3.46 g, 25 mmol) in DMF (50 mL), 6.1 g (76%) of methyl 3,4,5-tris-(heptadecafluoro-dodecyloxy) benzoate was obtained as a white solid. The ester (4.0 g, 2.5 mmol) was then hydrolyzed with excess KOH (0.7 g, 12.5 mmol) in refluxing ethanol (95%, 25 mL). After refluxing for 2h, the reaction mixture was cooled to room temperature and its THF solution was acidified with dilute HCl to pH 1. The solution was poured into ice-cooled water (200 mL) and the precipitated solid was collected under vacuum filtration. Recrystallization from acetone yielded 3.6 g (90%) of white solid. Purity (HPLC): 99+%; TLC (EtOAc/hexane = 3/7): R_f = 0.09 - 0.3; ^{1}H NMR (500 MHz, acetone-d6, 30 °C, TMS): δ = 1.95 (m, 12H, $CF_2(CH_2)_2$), 2.4 (m, 6H, CH_2CH_2O), 4.1 (t, 2H, CH_2O, 4 position, J = 5.55 Hz), 4.18 (t, 4H, CH_2O, 3,5 position, J = 5.85), 7.34 (s, 2H, ArH); ^{19}F NMR (470 MHz, acetone-d6, 30 °C, TMS): δ = -81.5 (overlapped t, 9F, CF_3), -115.0 (m, 6F, CF_2CH_2), -122.4 (m, 18F, $(CF_2)_3CF_2CH_2$), -123.3 (s, 6F, $CF_3(CF_2)_2CF_2$), -124.1 (d, 6F, $CF_3CF_2CF_2$), -126.7 (d, 6F, CF_3CF_2); ^{13}C NMR (125 MHz, acetone-d6, 30 °C, TMS): δ = 18.1 ($CF_2CH_2CH_2$), 30.5 (CH_2CH_2OAr), 31.2 (overlapped t, CF_2CH_2), 69.3 (CH_2OAr, 3,5 position), 73.4 (CH_2OAr, 4 position), 109.1 (*ortho* to CO_2H), 125.7 (*ipso* to CO_2H), 142.2 (*para* to CO_2H), 153.7 (*meta* to CO_2H), 166.8 ($PhCO_2H$).

3,4,5-Tris-(heptadecafluoro-dodecyloxy)-*N*-[3,4,5-tris-(heptadecafluoro-dodecyloxy)-phenyl] benzamide (10). A 50 mL 3-neck round-bottom flask containing a

teflon-coated magnetic stir bar was charged with compounds **8** (235 mg, 0.15 mmol), **9** (240 mg, 0.15 mmol), DCC (60 mg, 0.3 mmol), DPTS (7 mg, 0.025 mmol) and dry α,α,α-trifluorotoluene (15 mL). The reaction mixture was stirred under argon for 4 h at 50 °C during which time the reaction was completed (monitored by TLC). The solvent was removed under reduced pressure at 40 °C. The solid was dissolved in a hot mixture of CH_2Cl_2/CFC-113, filtered and passed through a short column of silica gel using CH_2Cl_2 as an eluent. The solvent was removed in a rotary evaporator and after precipitation in methanol twice, 300 mg (62 %) of **10** was obtained as a white solid. Purity (HPLC): 99%; thermal transitions and the corresponding enthalpy changes are summarized in Table 1. TLC (EtOAc/hexane = 3/7): R_f = 0.67; ^{1}H NMR (500 MHz, THF-d8, 45 °C): δ = 1.89 (overlapped m, 24H, $(CH_2)_2CF_2$), 2.26 (m, 12H, $CH_2(CH_2)_2CF_2$), 3.96-4.13 (overlapped t, 12H, CH_2OPh), 7.13 (s, 2H, *ortho* to NHCO), 7.23 (s, 2H, *ortho* to CONH), 8.86 (s, 1H, NH); ^{19}F NMR (470 MHz, THF-d8, 45 °C,): δ = -82.3 (overlapped t, 18F, CF_3), -115.1 (m, 12F, CF_2CH_2), -122.7 (m, 36F, $(CF_2)_3CF_2CH_2$), -123.5 (s, 12F, $CF_3(CF_2)_2CF_2$), -124.2 (s, 12F, $CF_3CF_2CF_2$), -127.1 (s, 12F, CF_3CF_2); ^{13}C NMR (125 MHz, THF-d8, 45 °C): δ= 18.5 ($CH_2CH_2CF_2$) 29.9 (CH_2CH_2OPh, 3,5 position), 30.8 (CH_2CH_2OPh, 4 position), 31.6 (CH_2CF_2), 69.7 (CH_2OPhCO, 3,5 position), 69.9 (CH_2OPhNH, 3,5 position), 73.4 (CH_2OPhCO, 4 position), 73.5 (CH_2OPhNH, 4 position), 101.0 (*ortho* to NHCO), 108.1 (*ortho* to CONH), 112.5 (CF_2), 132.1 (*para* to NHCO), 136.0 (*ipso* to CONH), 136.6 (*ipso* to NHCO, *para* to CONH), 153.9 (*meta* to NHCO and CONH), 165.7 (CONH); MALDI-TOF *m/z*: 3138.70 (M^+, calculated 3138.16), 1360.55 ($[M+Na]^+$, calculated 3161.15).



Reagents and conditions: i) DCC, DPTS, α,α,α-trifluorotoluene, 50 °C, 4 h; ii) n-BuLi, THF, CH_3I, 0-22 °C, 3h.

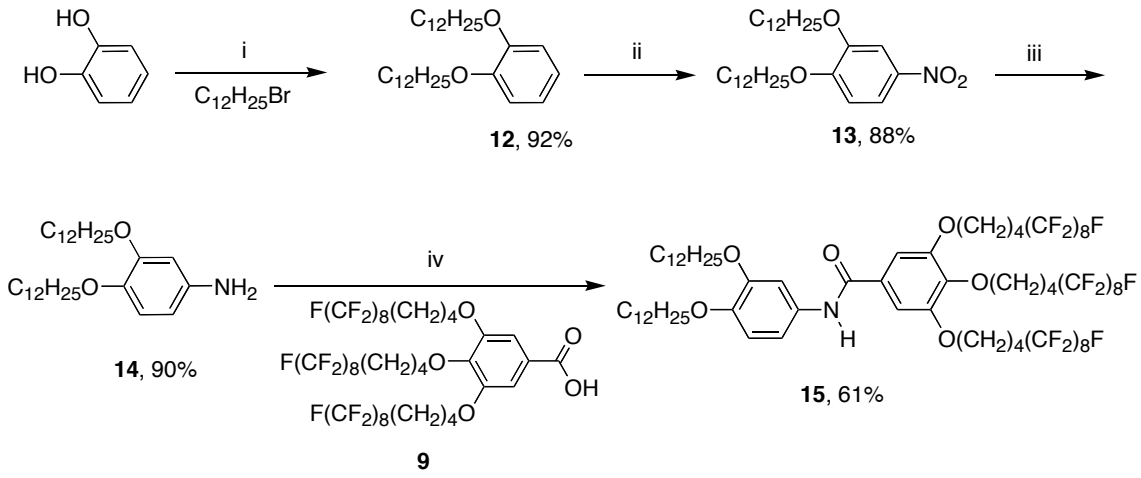
Scheme 3 (supporting). Synthesis of (3,4,5)12G1-(3,4,5)12F8G1-benzamide (**11**) and its -NCH_3 derivative (**11a**)

3,4,5-Tris-(heptadecafluoro-dodecyloxy)-*N*-(3,4,5-tris-dodecyloxy-phenyl)benzamide (11). Compound **11** was synthesized by the same procedure described for the preparation of **10**. From **3** (325 mg, 0.5 mmol), and **9** (796 mg, 0.5 mmol) in α,α,α-trifluorotoluene (10 mL) containing DCC (205 mg, 1mmol) and DPTS (15 mg, 0.05 mmol) 740 mg (66.7%) of white solid was obtained. Purity (HPLC), 99%; thermal transitions and the corresponding enthalpy changes are summarized in Table 1. TLC (EtOAc/hexane = 1/9): R_f = 0.89; ^{1}H NMR (500 MHz, $CDCl_3$, 30 °C, TMS): δ = 0.88 (overlapped t, 9H, CH_3), 1.26 (overlapped m, 48H, $(CH_2)_8$), 1.46 (m, 6H, $CH_2CH_2CH_2OPhNH$), 1.72-1.94 (overlapped m, 18H, CH_2CH_2OPhNH and $(CH_2)_2CF_2$), 2.16 (m, 6H, $CH_2(CH_2)_2CF_2$), 3.92-4.03 (overlapped t, 8H, CH_2OPhNH and CH_2OPhCO, 4 position), 4.08 (t, 4H, CH_2OPhCO, 3,5 position, *J* = 5.67), 6.89 (s, 2H, *ortho* to NHCO), 7.04 (s, 2H, *ortho* to CONH), 7.58 (s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$, 30 °C, TMS): δ = 14.3 (CH_3), 17.5 ($CH_2CH_2CF_2$, 4 position), 17.6 ($CH_2CH_2CF_2$, 3,5 position), 22.9 (CH_2CH_3), 26.3

($CH_2CH_2CH_2OPhNH$), 29.0 (CH_2CH_2OPhCO), 29.5-30.7 (CH_2CH_2OPhNH, $(CH_2)_6CH_2CH_2CH_3$), 30.8 (CH_2CF_2) 32.2 ($CH_2CH_2CH_3$), 68.9 (CH_2OPhCO, 3,5 position), 69.5 (CH_2OPhNH, 3,5 position), 73.0 (CH_2OPhCO, 4 position), 73.8 (CH_2OPhNH, 4 position), 99.5 (*ortho* to NHCO), 106.1 (*ortho* to CONH), 130.8 (*ipso* to CONH), 133.6 (*para* to NHCO), 135.5 (*ipso* to NHCO), 141.3 (*para* to CONH), 153.2, 153.5 (*meta* to NHCO and CONH), 165.7 (CONH); ^{19}F NMR (470 MHz, $CDCl_3$, 30 °C, TMS): δ = -81.3 (overlapped t, 9F, CF_3), -114.9 (m, 6F, CF_2CH_2), -122.3 (m, 18F, $(CF_2)_3CF_2CH_2$), -123.2 (s, 6F, $CF_3(CF_2)_2CF_2$), -123.9 (m, 6F, $CF_3CF_2CF_2$), -126.6 (m, 6F, CF_3CF_2); MALDI-TOF *m/z*: 2220.81 (M^+, calculated 2220.63), 2242.84 ($[M+Na]^+$, calculated 2243.62).

***N*-Methyl-3,4,5-tris-(heptadecafluoro-dodecyloxy)-*N*-(3,4,5-tris-dodecyloxy-phenyl) benzamide (11a).** To a stirred solution of **11** (220 mg, 0.1 mmol) in dry THF (6 mL) at 0 °C, nBuLi (60 μL, 0.15 mmol) was added dropwise under Ar. To the solution, CH_3I (6 μL, 0.1 mmol) was added slowly through a microsyringe and stirred for 15 min. The reaction mixture was stirred at 22 °C for 3 h. after which was added slowly to cold water (20 mL) and stirred for 10 min. The precipitated solid was collected by filtration. Purification of the crude product by column chromatography (SiO_2, EtOAc/hexane, 2/8) and precipitation in cold MeOH yielded 185 mg (83%) of **11a** as a slightly tan colored powder. Purity (HPLC), 99%; thermal transitions and the corresponding enthalpy changes are shown in Figure 4 (supporting). TLC (EtOAc/hexane = 3/7): R_f = 0.52; ^1H NMR (500 MHz, $CDCl_3$, 30 °C, TMS): δ = 0.88 (t, 9H, CH_3, *J* = 6.7 Hz), 1.26 (overlapped m, 48H, $(CH_2)_8$), 1.42 (m, 6H, $CH_2CH_2CH_2OPhNCH_3$), 1.67-1.76 (overlapped m, 18H, $CH_2CH_2OPhNCH_3$ and $(CH_2)_2CF_2$), 2.12 (m, 6H, $CH_2(CH_2)_2CF_2$),

3.44 (s, 3H, NCH_3), 3.92-4.03 (overlapped t, 8H, $CH_2OPhNCH_3$ and CH_2OPhCO, 4 position), 3.87 (overlapped t, 4H, CH_2OPhCO, 3,5 position), 6.24 (s, 2H, *ortho* to NCH_3CO), 6.60 (s, 2H, *ortho* to $CONCH_3$); ^{13}C NMR (125 MHz, CDCl3, 30 °C, TMS): δ = 14.3 (CH_3), 17.5 ($CH_2CH_2CF_2$, 4 position), 17.6 ($CH_2CH_2CF_2$, 3,5 position), 22.9 (CH_2CH_3), 26.3 ($CH_2CH_2CH_2OPhNCH_3$), 28.9 (CH_2CH_2OPhCO), 29.4-30.6 ($CH_2CH_2OPhNCH_3$, $(CH_2)_6CH_2CH_2CH_3$), 30.8 (CH_2CF_2) 32.1 ($CH_2CH_2CH_3$), 38.9 (NCH_3), 68.5 (CH_2OPhCO, 3,5 position), 69.6 ($CH_2OPhNCH_3$, 3,5 position), 72.7 (CH_2OPhCO, 4 position), 73.8 ($CH_2OPhNCH_3$, 4 position), 106.0 (*ortho* to $CONCH_3$), 108.1 (*ortho* to NCH_3CO), 131.1 (*ipso* to $CONCH_3$), 137.3 (*para* to NCH_3CO), 139.3 (*ipso* to NCH_3CO), 140.7 (*para* to $CONCH_3$), 152.2 (*meta* to NCH_3CO), 153.5 (*meta* to $CONCH_3$), 169.8 ($CONCH_3$); ^{19}F NMR (470 MHz, CDCl3, 30 °C, TMS): δ = -81.3 (overlapped t, 9F, CF_3), -115.0 (m, 6F, CF_2CH_2), -122.3 (m, 18F, $(CF_2)_3CF_2CH_2$), -123.3 (s, 6F, $CF_3(CF_2)_2CF_2$), -123.9 (m, 6F, $CF_3CF_2CF_2$), -126.7 (m, 6F, CF_3CF_2); MALDI-TOF *m/z*: 2234.83 (M^+, calculated 2234.68), 2256.92 ($[M+Na]^+$, calculated 2257.67).



Reagents and conditions: i) K_2CO_3, DMF, 70 °C, 6 h; ii) $SiO_2 \cdot HNO_3$, CH_2Cl_2, 25 °C, 12 h; iii) $NH_2NH_2 \cdot H_2O$, graphite, EtOH, reflux, 24 h; iv) DCC, DPTS, α,α,α-trifluorotoluene, 50 °C, 4 h.

Scheme 4 (supporting). Synthesis of (3,4)12G1-(3,4,5)12F8G1-benzamide (**15**)

1,2-Bis-dodecyloxy-benzene (12). Compound **12** was synthesized by the same general procedure described for the synthesis of compound **1**. From dihydroxybenzene (11.0 g, 0.1 mol), 1-bromododecane (50.8 g, 0.2 mol) and anhydrous K_2CO_3 (70 g, 0.5 mol) in DMF (200 mL), 41 g (92%) of **12** was obtained as a white solid, after recrystallization from acetone. Purity (HPLC): 99%; m.p. 41-42 °C; TLC (EtOAc/hexane = 3/7): R_f = 0.90; ^{1}H NMR (500 MHz, $CDCl_3$, 30 °C, TMS): δ = 0.88 (t, 6H, CH_3, J = 6.8 Hz), 1.31 (overlapped m, 32H, $(CH_2)_8$), 1.47 (m, 4H, $CH_2CH_2CH_2OPh$), 1.80 (m, 4H, CH_2CH_2OPh), 3.99 (t, 4H, CH_2OPh, J = 6.6), 6.89 (overlapped s, 4H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$, 30 °C): δ = 14.3 (CH_3), 22.9 (CH_2CH_3), 26.3 ($CH_2CH_2CH_2OPh$), 29.7 (CH_2CH_2OPh, $(CH_2)_6$), 32.1 ($CH_2CH_2CH_3$), 69.6 (CH_2OPh), 114.6 (3,6 position on Ar), 121.3 (4,5 position on Ar), 149.6 (1,2 position on Ar).

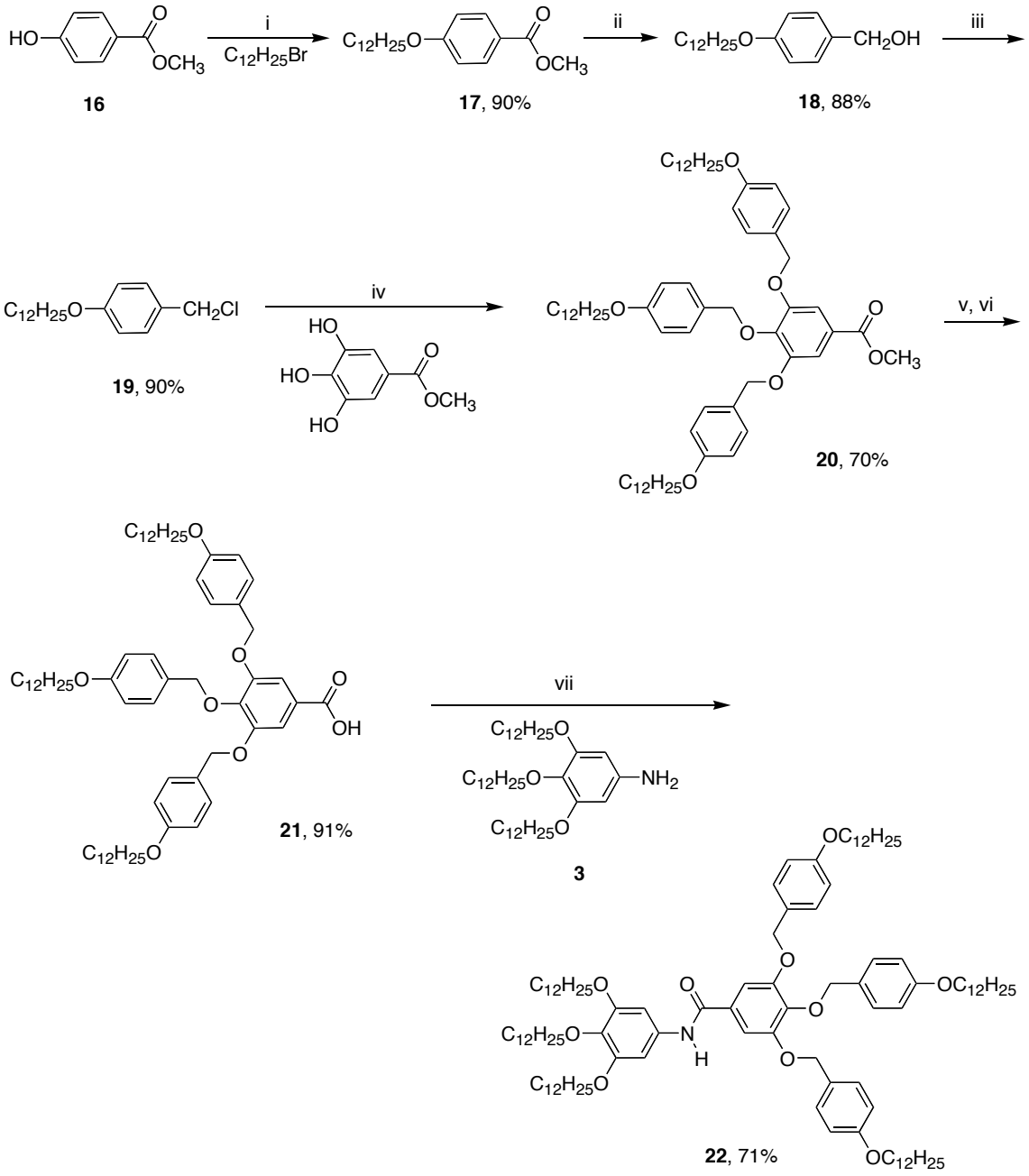
1,2-Bis-dodecyloxy-4-nitrobenzene (13) Compound **13** was synthesized by the same general procedure described for the synthesis of compound **2**. From compound **12** (20 g, 44.8 mmol) and $SiO_2{\cdot}HNO_3$ (33.8 g, 89.6 mmol) in CH_2Cl_2 (400 mL), recrystallization from acetone produced 19.4 g (88%) of **12** as a white solid. Purity (HPLC): 99%; m.p. 68-69 °C; TLC (EtOAc/hexane = 3/7): R_f = 0.88; ^{1}H NMR (500 MHz, $CDCl_3$, 30 °C, TMS): δ = 0.88 (t, 6H, CH_3, *J* = 6.8 Hz), 1.27 (overlapped m, 32H, $(CH_2)_8$), 1.48 (m, 4H, $CH_2CH_2CH_2OPh$), 1.85 (m, 4H, CH_2CH_2OPh), 4.07 (m, 4H, CH_2OPh), 6.86 (d, 1H, 6 position on Ar, *J* = 8.95), 7.73 (d, 1H, 3 position on Ar, *J* = 2.6), 7.86 (dd, 1H, 5 position on Ar, *J* = 2.6, 6.3); ^{13}C NMR (125 MHz, $CDCl_3$, 20 °C): δ = 14.3 (CH_3), 22.9 (CH_2CH_3), 26.1 ($CH_2CH_2CH_2OPh$), 29.6 (CH_2CH_2OPh, $(CH_2)_6$), 32.1 ($CH_2CH_2CH_3$), 69.7, 69.8 (CH_2OPh), 108.5 (3 position on Ar), 111.4 (5 position on Ar), 117.9 (6 position on Ar), 141.3 (4 position on Ar, *ipso* to NO_2), 148.9 (2 position on Ar), 154.9 (1 position on Ar, *para* to NO_2).

3,4-Bis-dodecyloxyphenylamine (14) Compound **14** was synthesized by the same general procedure described for the synthesis of compound **3**. From compound **13** (4.9 g, 10 mmol), graphite (4 g) and $NH_2NH_2{\cdot}H_2O$ (1.5 mL, 30 mmol) in ethanol (75 mL), recrystallization from acetone produced 4.2 g (90%) of **13** as a white solid. Purity (HPLC): 99%; m.p. 50-51 °C; TLC (EtOAc/hexane = 3/7): R_f = 0.41; ^{1}H NMR (500 MHz, $CDCl_3$, 30 °C, TMS): δ = 0.88 (t, 6H, CH_3, *J* = 6.8 Hz), 1.32 (overlapped m, 32H, $(CH_2)_8$), 1.45 (m, 4H, $CH_2CH_2CH_2OPh$), 1.76 (m, 4H, CH_2CH_2OPh), 3.41 (bs, 2H, NH_2), 3.92 (overlapped t, 4H, CH_2OPh), 6.20 (q, 1H, 6 position on Ar, *J* = 2.65, 5.7), 6.30 (d, 1H, 2 position on Ar, *J* = 2.6), 6.73 (d, 1H, 5 position on Ar, *J* = 8.4); ^{13}C NMR (125 MHz, $CDCl_3$, 30 °C, TMS): δ = 14.3 (CH_3), 22.9 (CH_2CH_3), 26.3 ($CH_2CH_2CH_2OPh$),

29.7 (CH_2CH_2OPh, $(CH_2)_6$), 32.1 ($CH_2CH_2CH_3$), 69.3 (CH_2OPh, 4 position), 71.3 (CH_2OPh, 3 position), 103.1 (2 position on Ar), 107.2 (6 position on Ar), 117.7 (5 position on Ar), 141.3 (1 position on Ar), 142.2 (4 position on Ar), 150.9 (3 position on Ar).

***N*-(3,4-Bis-dodecyloxy-phenyl)-3,4,5-tris-(heptadecafluoro-dodecyloxy)benzamide (15).** Compound **15** was synthesized by the same procedure described for the preparation of **10**. From **14** (462 mg, 1 mmol), and **9** (1.6 g, 1 mmol) in α,α,α-trifluorotoluene (20 mL) containing DCC (410 mg, 2 mmol) and DPTS (57 mg, 0.2 mmol), 1.24 g (61%) of white solid was obtained. Purity (HPLC), 99%; thermal transitions and the corresponding enthalpy changes are summarized in Table 1. TLC (EtOAc/hexane = 3/7): R_f = 0.76; ^{1}H NMR (500 MHz, $CDCl_3$, 30 °C, TMS): δ= 0.88 (overlapped t, 6H, CH_3), 1.27 (overlapped m, 32H, $(CH_2)_8$), 1.46 (m, 4H, $CH_2CH_2CH_2OPhNH$), 1.81-2.16 (overlapped m, 16H, CH_2CH_2OPhNH and $(CH_2)_2CF_2$), 2.17 (m, 6H, $CH_2(CH_2)_2CF_2$), 3.97-4.03 (overlapped t, 6H, CH_2OPhCO), 4.09 (t, 4H, CH_2OPhNH, *J* = 5.6 Hz), 6.86 (d, 1H, 5 position on Ar-NHCO, *J* = 8.6), 6.94 (dd, 1H, 6 position on Ar-NHCO, *J* = 2.4. 6.2), 7.05 (s, 2H, *ortho* to CONH), 7.43 (s, 1H, 2 position on Ar-NHCO), 7.59 (s, 1H, NH); ^{19}F NMR (470 MHz, $CDCl_3$, 30 °C, TMS): δ = -81.3 (overlapped t, 9F, CF_3), -114.8 (m, 6F, CF_2CH_2), -122.3 (m, 18F, $(CF_2)_3CF_2CH_2$), -123.2 (s, 6F, $CF_3(CF_2)_2CF_2$), -123.9 (d, 6F, $CF_3CF_2CF_2$), -126.6 (m, 6F, CF_3CF_2); ^{13}C NMR (125 MHz, $CDCl_3$, 30 °C, TMS): δ = 14.3 (CH_3), 17.4 ($CF_2CH_2CH_2$, 4 position), 17.6 ($CF_2CH_2CH_2$, 3,5 position), 22.9 (CH_2CH_3), 26.3 ($CH_2CH_2CH_2OPhNH$), 29.0 (CH_2CH_2OPhCO), 29.7 (CH_2CH_2OPhNH), 29.9 (($CH_2)_6$), 30.9 (t, CF_2CH_2), 32.1 ($CH_2CH_2CH_3$), 69.0 (CH_2OPhCO, 3,5 position), 69.6 (CH_2OPhNH, 4 position), 70.2 (CH_2OPhNH, 3 position), 73.0 (CH_2OPhCO, 4

position), 106.2 (*ortho* to CONH), 107.6 (2 position on ArNH), 112.6 (6 position on ArNH), 115.0 (5 position on ArNH), 130.9 (*ipso* to CONH), 131.9 (*ipso* to NHCO), 141.3 (*para* to CONH), 146.9 (4 position on ArNH), 149.9 (3 position on ArNH), 153.2 (*meta* to CONH), 165.3 (CONH); MALDI-TOF *m*/*z*: 2035.87 (M^+, calculated 2036.34), 2058.49 ($[M+Na]^+$, calculated 2059.33).



Reagents and conditions: i) K_2CO_3, DMF, 70 °C, 6 h; ii) $LiAlH_4$, THF, 0 °C-r.t. 2 h; iii) $SOCl_2$, CH_2Cl_2, DMF (catalytic), 20 °C, 1/2 h; iv) K_2CO_3, DMF, 65 °C, 6 h; v) KOH, EtOH (95%), reflux, 2 h; vi) THF, H_3O^+; vii) DCC, DPTS, CH_2Cl_2, 25 °C, 24 h.

Scheme 5 (supporting). Synthesis of (3,4,5)12G1-(4-3,4,5)12G1-BzA (**22**).

Methyl-4-dodecyloxybenzoate (17): To a thoroughly degassed suspension of anhydrous K_2CO_3 (277 g, 2.0 mole) in DMF (800 mL) was added methyl-4-hydroxybenzoate (**16**) (76.1 g, 0.50 mole) and the reaction mixture was heated to 70 °C which was added 1-bromododecane (125.0 g, 0.50 mole) under Ar in small portions over 15 min. After stirring for 4 h at 70 °C, the reaction mixture was poured into stirring ice/water (2L). The white granular solid was filtered and washed with H_2O. Recrystallization from acetone yielded 144 g (90%) of white sheet-like crystals. Purity (HPLC): 99+%; m.p. 53-55 °C (ref. [5]: 56-57 °C); TLC (EtOAc/hexane = 1/9): R_f = 0.59; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (t, 3H, CH_3, *J* = 6.8 Hz), 1.27-1.35 (overlapped peaks, broad, 16H, $CH_3(CH_2)_8$), 1.44-1.46 (m, 2H, $CH_2(CH_2)_2O$), 1.78-1.8 (m, 2H, CH_2CH_2O), 3.88 (s, 3H, CO_2CH_3), 4.0 (t, 2H, CH_2OAr, *J* = 6.6), 6.89 (d, 2H, 3,5 position, *J* = 8.6), 7.97 (d, 2H, 2,6 position, *J* = 8.8); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.3 (CH_3), 22.9 (CH_3CH_2), 26.2 ($CH_2CH_2CH_2O$), 29.3 ($CH_3CH_2CH_2CH_2$), 29.7 ($CH_3CH_2CH_2CH_2(CH_2)_5$), 29.8 (CH_2CH_2O), 32.1 ($CH_3CH_2CH_2$), 52.0 (CO_2CH_3), 68.5 (CH_2O), 114.3 (3,5 position), 122.6 (1 position), 131.8 (2,6 position), 163.2 (4 position), 167.1 ($ArCO_2CH_3$).

4-Dodecyloxybenzyl alcohol (18): The title compound **18** was synthesized according to a general procedure developed for the $LiAlH_4$ reduction of methyl alkoxybenzoates. [7] To a stirred suspension of $LiAlH_4$ (11.3 g, 0.3 mole) in dry THF (300 mL) at 0 °C was added slowly methyl 4-dodecyloxybenzoate, **17** (64.1 g, 0.2 mole) in dry THF (200 mL) under Ar over a period of 30 min. After complete addition, the reaction mixture was allowed to warm to room temperature and stirred for 2 h, after which TLC showed completion. The reaction was quenched by successive addition of H_2O (25 mL), 15% aq. NaOH (25 mL), and H_2O (75 mL) with continuous stirring until H_2 evolution ceased. The reaction mixture

was filtered and the lithium salt was washed with CH_2Cl_2. The filtrate was dried over $MgSO_4$ and the solvent was removed in a rotary evaporator. Recrystallization from acetone yielded 51.5 g (88%) of white crystals. Purity (HPLC): 99+%; m.p. 65-67 °C (ref. [7]): 66-68 °C); TLC (EtOAc/hexane = 3/7): R_f = 0.53; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (t, 3H, CH_3, *J* = 6.8 Hz), 1.27-1.34 (overlapped peaks, broad, 16H, $CH_3(CH_2)_8$), 1.43 (m, 2H, $CH_2(CH_2)_2O$), 1.50 (s, 1H, OH), 1.75-1.78 (m, 2H, CH_2CH_2O), 3.95 (t, 2H, CH_2OAr, *J* = 6.6), 4.60 (d, 2H, $ArCH_2OH$, *J* = 5.8), 6.88 (d, 2H, 3,5 position, *J* = 8.6), 7.27 (d, 2H, 2,6 position, *J* = 8.5); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.3 (CH_3), 22.9 (CH_3CH_2), 26.2 ($CH_2CH_2CH_2O$), 29.5 ($CH_3CH_2CH_2CH_2$), 29.6 ($CH_3CH_2CH_2CH_2(CH_2)_5$), 29.8 (CH_2CH_2O), 32.1 ($CH_3CH_2CH_2$), 65.4 ($ArCH_2OH$), 68.4 (CH_2O), 114.9 (2,6 position), 128.8 (3,5 position), 133.2 (4 position), 159.1 (1 position).

4-Dodecyloxybenzyl chloride (19): A two-neck round bottom flask equipped with a Teflon-coated magnetic stirrer and an addition funnel was charged with 4-dodecyloxybenzyl alcohol, **18** (43.9 g, 0.15 mole) in dry CH_2Cl_2 (400 mL) and a catalytic amount of DMF. The reaction flask was flushed with Ar, and cooled in an ice bath at 0°C. Thionyl chloride (13.2 mL, 0.18 mole) in dry CH_2Cl_2 (50 mL) was added dropwise to the cooled reaction mixture. After complete addition, the reaction mixture was stirred at room temperature for 30 min. The solvent was removed by vacuum distillation and the residue was recrystallized from hexane to yield 42.0 g (90%) of needle like crystals. Purity (HPLC): 99+%; m.p. 37-39 °C; TLC (EtOAc/hexane = 3/7): R_f = 0.85; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (t, 3H, CH_3, *J* = 6.8 Hz), 1.27-1.34 (overlapped peaks, broad, 16H, $CH_3(CH_2)_8$), 1.43-1.46 (m, 2H, $CH_2(CH_2)_2O$), 1.75-1.78 (m, 2H, CH_2CH_2O), 3.95 (t, 2H, CH_2OAr, *J* = 6.6), 4.56 (s, 2H, $ArCH_2Cl$), 6.87 (d, 2H, 3,5

position, J = 8.6), 7.29 (d, 2H, 2,6 position, J = 8.5); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.3 (CH_3), 22.8 (CH_3CH_2), 26.2 ($CH_2CH_2CH_2O$), 29.5 ($CH_3CH_2CH_2CH_2$), 29.7 ($CH_3CH_2CH_2CH_2(CH_2)_5$), 29.8 (CH_2CH_2O), 32.1 ($CH_3CH_2CH_2$), 46.5 ($ArCH_2Cl$), 68.2 (CH_2O), 114.8 (2,6 position), 129.6 (3,5 position), 130.2 (1 position), 159.5 (4 position).

Methyl 3,4,5-tris-(4-dodecyloxy-benzyloxy)benzoate (20): Compound **20** was synthesized by the same general procedure described for the synthesis of compound 1**7**. From methyl 3,4,5-trihydroxybenzoate, **16** (3.68 g, 0.02 mole), K_2CO_3 (16.5 g, 0.12 mole), and 4-dodecyloxybenzyl chloride, **19** (18.65 g, 0.06 mole) in DMF (100 mL) for 6 h at 70 °C, 14.1 g (70%) of a white solid was obtained after passing through a short column of basic Al_2O_3 using CH_2Cl_2 as eluent followed by recrystallization from acetone. Purity (HPLC): 99+%; TLC (EtOAc/hexane = 1/9): R_f = 0.36; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (t, 9H, CH_3, J = 6.3 Hz), 1.27-1.32 (overlapped m, 48H, $CH_3(CH_2)_8$), 1.43-1.46 (m, 6H, $CH_2(CH_2)_2O$), 1.76-1.81 (m, 6H, CH_2CH_2O), 3.89 (s, 3H, CO_2CH_3), 3.96 (t, 6H, CH_2OAr, J = 6.4), 5.00 (s, 2H, $ArCH_2$, 4 position), 5.03 (s, 4H, $ArCH_2$, 3,5 position), 6.75 (d, 2H, ArH, *meta* to $ArOCH_2$, 4 position, J = 8.3), 6.89 (d, 4H, ArH, *meta* to $ArOCH_2$, 3,5 position, J = 8.4), 7.25 (d, 2H, ArH, *ortho* to $ArOCH_2$, 4 position, J = 8.5), 7.33 (d, 4H, ArH, *ortho* to $ArOCH_2$, 3.5 position, J = 8.3), 7.36 (s, 2H, ArH, *ortho* to CO_2CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.3 (CH_3), 22.9 (CH_3CH_2), 26.3 ($CH_2CH_2CH_2O$), 29.5-29.9 ($CH_3CH_2CH_2(CH_2)_6$, CH_2CH_2O), 32.1 ($CH_3CH_2CH_2$), 52.3 (CO_2CH_3), 68.3 (CH_2O, 3,4,5 position), 71.4 ($ArCH_2OAr$, 3,5 position), 74.9 ($ArCH_2OAr$, 4 position), 109.6 (*ortho* to CO_2CH_3), 114.4 (*meta* to CH_2OAr, 4 position), 114.7 (*meta* to CH_2OAr, 3,5 position), 125.3 (*ipso* to CO_2CH_3),

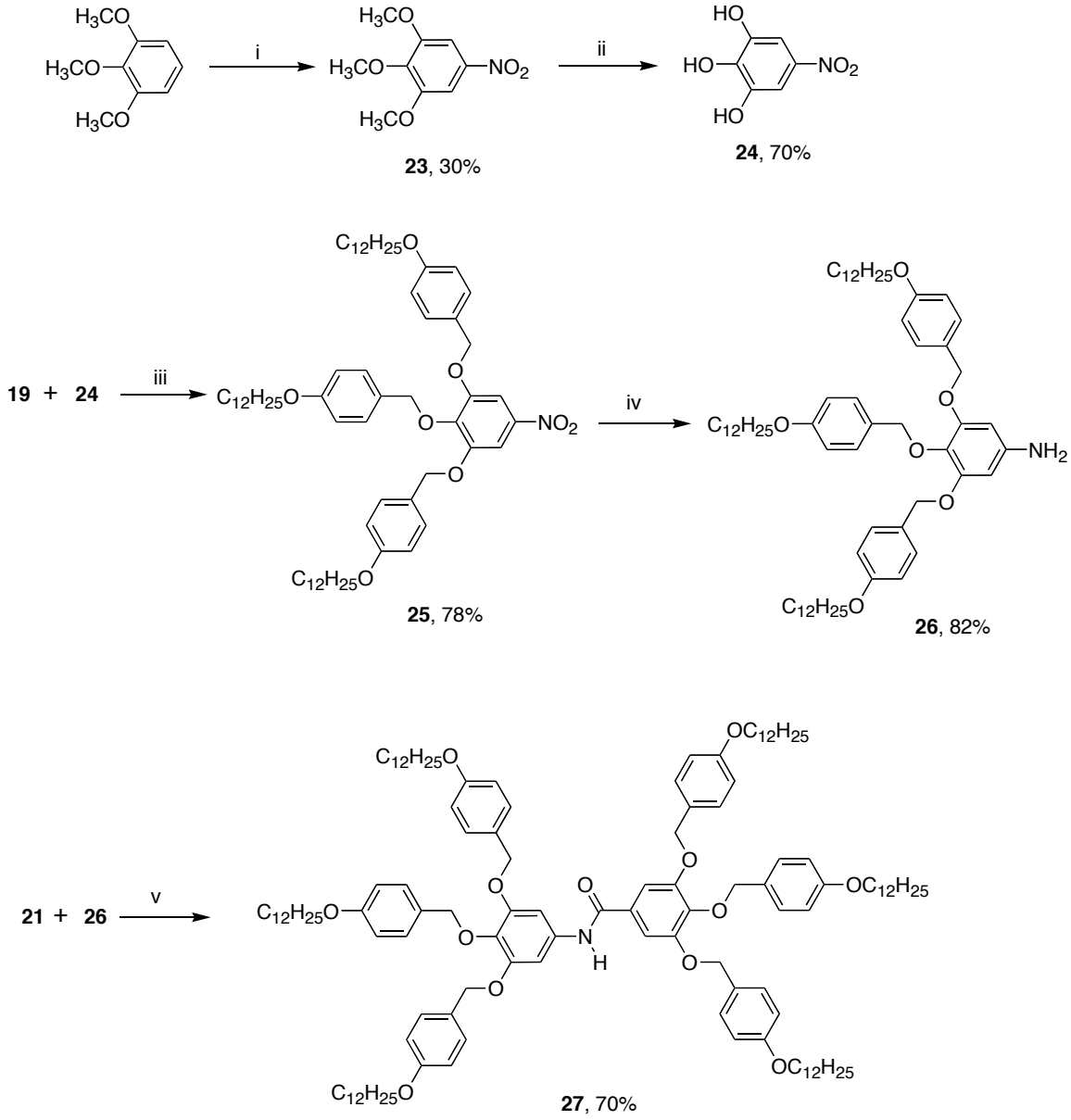
128.9 (*ipso* to CH_2OAr, 3,4,5 position), 129.5 (*ortho* to CH_2OAr, 3,5 position), 130.4 (*ortho* to CH_2OAr, 4 position), 142.9 (*para* to CO_2CH_3), 152.9 (*meta* to CO_2CH_3), 159.3 (*para* to CH_2OAr, 3,4,5 position), 166.9 ($ArCO_2CH_3$).

3,4,5-Tris-(4-dodecyloxy-benzyloxy)benzoic acid (21). Compound **21** was synthesized according to a modified literature procedure.[7,8] Compound **20** (10.1 g, 10 mmol), EtOH (100 mL, 95%), and KOH solution (3 g, dissolved in 10 mL of H_2O) were placed into a 500 mL round-bottom flask containing a Teflon coated magnetic stirring bar and heated to reflux for 2 h under constant stirring. After the reaction was completed it was cooled to 22 °C and diluted with THF (160 mL). The solution was acidified with glacial CH_3COOH, then with dilute HCl to pH 3. The solution was poured into 400 mL ice/water and stirred for 15 min. The precipitated solid was collected by filtration and dried. The solid was dissolved in a minimum volume of CH_2Cl_2 and precipitated in CH_3OH to yield 9.0 g (91%) of white powder. Purity (HPLC): 99+%; m.p. 147 °C (isotropic); TLC (EtOAc/hexane = 3/7): R_f = 0.38; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (t, 9H, CH_3, *J* = 6.5 Hz), 1.27-1.30 (overlapped m, 48H, $CH_3(CH_2)_8$), 1.41 (m, 6H, $CH_2(CH_2)_2O$), 1.70-1.76 (m, 6H, CH_2CH_2O), 3.86 (t, 6H, CH_2OAr, *J* = 6.4 Hz), 4.83 (overlapped s, 6H, $ArCH_2$), 6.65 (d, 2H, ArH, *meta* to $ArOCH_2$, 4 position, *J* = 7.8), 6.75 (d, 4H, ArH, *meta* to $ArOCH_2$, 3,5 position, *J* = 7.0), 7.13 (d, 2H, ArH, *ortho* to $ArOCH_2$, 4 position, *J* = 7.0), 7.18 (d, 4H, ArH, *ortho* to $ArOCH_2$, 3.5 position, *J* = 7.1), 7.37 (s, 2H, ArH, *ortho* to CO_2H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.3 (CH_3), 22.9 (CH_3CH_2), 26.3 ($CH_2CH_2CH_2O$), 29.6-29.9 ($CH_3CH_2CH_2(CH_2)_6$, CH_2CH_2O), 32.2 ($CH_3CH_2CH_2$), 68.2 (CH_2O, 3,4,5 position), 71.1 ($ArCH_2OAr$, 3,5 position), 74.9 ($ArCH_2OAr$, 4 position), 109.5 (*ortho* to CO_2H), 114.2 (*meta* to CH_2OAr, 4 position),

114.5 (*meta* to CH_2OAr, 3,5 position), 128.8 (*ipso* to CO_2H), 129.6 (*ipso* to CH_2OAr, 3,4,5 position), 129.9 (*ortho* to CH_2OAr, 3,5 position), 130.2 (*ortho* to CH_2OAr, 4 position), 152.8 (*para* to CO_2H), 159.1 (*meta* to CO_2H), 159.2 (*para* to CH_2OAr, 3,4,5 position), 171.9 ($ArCO_2H$).

3,4,5-Tris-(4-dodecyloxy-benzyloxy)-*N*-(3,4,5-tris-dodecyloxy-phenyl)benzamide (22). The acid **21** (993 mg, 1 mmol), amine **3** (646 mg, 1 mmol), DCC (412 mg, 2 mmol), DPTS (15 mg, 0.05 mmol), and dry CH_2Cl_2 (20 mL) were all combined in a 100 mL two-neck flask with a magnetic stirring bar under Ar. The reaction mixture was stirred for 24 h at room temperature. After the reaction was completed, the reaction mixture was poured into MeOH. The precipitated solid was collected by vacuum filtration and dried. Purification of the crude product by column chromatography (silica gel, EtOAc/hexane, 3/7) and precipitation in cold methanol yielded 1.15 g (71%) of the title compound as pale white solid. Purity (HPLC), 99+%; thermal transitions and the corresponding enthalpy changes are summarized in Table 1; TLC (EtOAc/hexane = 3/7): R_f = 0.90; ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C, TMS): δ = 0.88 (overlapped t, 18H, CH_3), 1.27-1.35 (overlapped m, 96H, $(CH_2)_8$), 1.46-1.51 (m, 12H, $CH_2(CH_2)_2O$), 1.76-1.80 (overlapped m, 12H, CH_2CH_2O), 3.91-4.00 (overlapped t, 12H, CH_2OAr), 5.02 (s, 2H, $ArCH_2$, 4 position), 5.06 (s, 4H, $ArCH_2$, 3,5 position), 6.77 (dd, 2H, ArH, *meta* to $ArOCH_2$, 4 position, J = 2.0, 6.8 Hz), 6.86 (s, 2H, *ortho* to CONH), 6.89 (dd, 4H, ArH, *meta* to $ArOCH_2$, 3,5 position, J = 2.1, 6.7), 7.10 (s, 2H, *ortho* to NHCO), 7.25 (d, 2H, ArH, *ortho* to $ArOCH_2$, 4 position, J = 8.7), 7.32 (d, 4H, ArH, *ortho* to $ArOCH_2$, 3,5 position, J = 8.7), 7.43 (s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C, TMS): δ = 14.3, 22.9, 26.4, 29.5-29.7, 29.8-30.0, 30.6, 32.1, 68.3, 68.4, 69.5, 71.8, 73.8, 75.0, 99.4, 107.6, 114.4,

114.8, 128.8, 129.5, 129.7, 130.4, 130.5, 133.7, 153.3, 153.5, 159.3, 159.4, 165.4 (CONH); MALDI-TOF *m*/*z*: 1621.66 (M^+, calculated 1621.51), 1644.28 ($[M+Na]^+$, calculated 1644.50).



Reagents and conditions: i) CH_2Cl_2, $SiO_2 \cdot HNO_3$, 22 °C, 15 min; ii) Py · HCl, 200 °C, 1 h; iii) K_2CO_3, DMF, 70 °C, 12 h; iv) $NH_2NH_2 \cdot H_2O$, graphite, EtOH, reflux, 24 h; v) CDMT, NMM, THF, 25 °C, 6 h.

Scheme 6 (supporting). Synthesis of (4-3,4,5)12G1-(4-3,4,5)12G1-BzA (**27**).

3,4,5-Trimethoxy-1-nitrobenzene (23). Compound **23** was synthesized according to a modified literature procedure.[8] To a stirred suspension of $SiO_2 \cdot HNO_3$ (118 g, 0.375 mol, 20% HNO_3 w/w) in CH_2Cl_2 (400 mL) at room temperature, 1,2,3-trimethoxybenzene (42 g, 0.25 mol) dissolved in CH_2Cl_2 (100 mL) was added rapidly. The resulting red solution was stirred for 15 min, filtered and washed several times with CH_2Cl_2. The solution was concentrated in a rotary evaporator and precipitated in cold MeOH (1 L). The yellow precipitate was collected by filtration and air-dried. Recrystallization from MeOH-CH_2Cl_2 yielded 16 g (30%) of **23** as yellowish-white crystals. Purity (HPLC): 99 %; m.p. 96-98 °C (ref. [8]): 98-99 °C); TLC (EtOAc/hexane = 3/7): R_f = 0.52; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 3.94 (s, 9H, CH_3OAr), 7.51 (s, 2H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 56.7, 61.3, 101.6, 144.1, 153.1.

3,4,5-Trihydroxy-1-nitrobenzene (24). Compound **24** was synthesized according to a literature procedure.[8] Compound **23** (6.4 g, 0.03 mol) was mixed with pyridine hydrochloride (21 g, 0.18 mol) and stirred at 200 °C for 1 h. The reaction mixture was cooled to below 100 °C and added to water. The solution was extracted with EtOAc three times. The combined extract was washed with dilute HCl, H_2O and finally with brine. The organic phase was dried over anhydrous $MgSO_4$ and evaporated to yield 3.6 g (70%) of **24** as yellow solid. The product was used for the next step without further purification. M.p. 194-196 °C (ref. [8]): 195-197 °C); ^{1}H NMR (500 MHz, DMSO-d6, 27 °C, TMS): δ = 7.21 (s, 2H, ArH), 9.77 (s, broad, 3H, OH); ^{13}C NMR (125 MHz, DMSO-d6, 27 °C, TMS): δ = 103.0, 138.5, 141.1, 145.4.

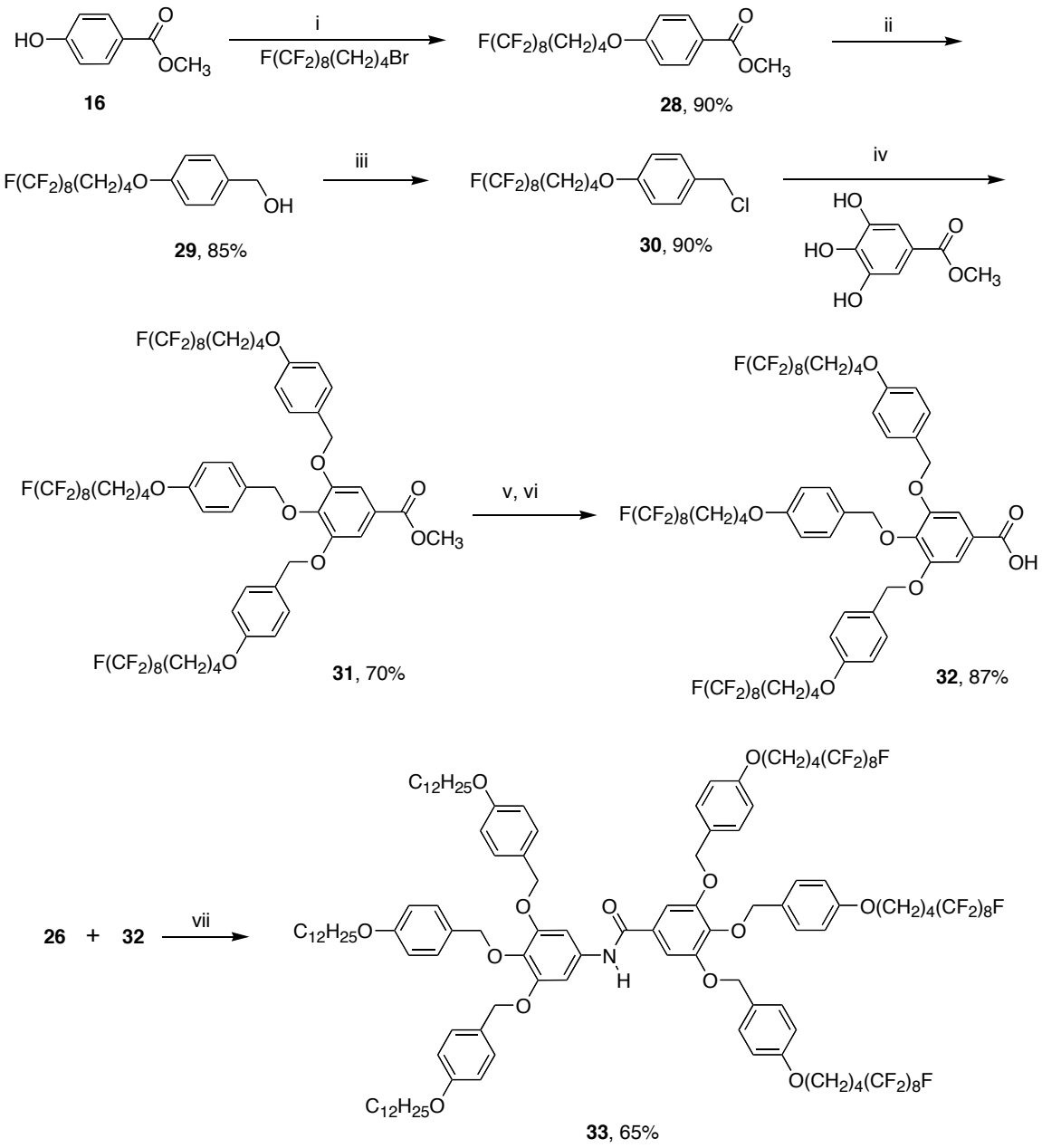
3,4,5-Tris-(4-dodecyloxy-benzyloxy)-1-nitrobenzene (25). Compound **25** was synthesized according to a literature procedure.[8] To a thoroughly degassed solution of

DMF (100 mL), compound **24** (1.71 g, 0.01 mol) and K_2CO_3 (8.3 g, 0.06 mol) were added under Ar and stirred for 10 min. After the addition of **19** (9.33 g, 0.03 mol), the reaction mixture was stirred at 70 °C overnight under Ar. The reaction mixture was cooled to room temperature and poured into ice/water (500 mL). The precipitate was collected by filtration and vacuum dried. The crude product was passed through a short column of basic Al_2O_3 using CH_2Cl_2 as eluent. The obtained product was purified by column chromatography (silica gel, EtOAc/hexane 1:9) and recrystallized from acetone to obtain 7.8 g (78%) of the title compound as a white powder. Purity (HPLC): 99+%; TLC (EtOAc/hexane = 2/8): R_f = 0.65; m.p. 76-77 °C (ref. [8]): 76-77 °C); ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (t, 9H, CH_3, *J* = 6.9 Hz), 1.27-1.34 (overlapped m, 48H, $CH_3(CH_2)_8$), 1.43-1.47 (m, 6H, $CH_2(CH_2)_2O$), 1.76-1.80 (m, 6H, CH_2CH_2O), 3.92 (t, 2H, CH_2OAr, 4 position, *J* = 6.6), 3.96 (t, 4H, CH_2OAr, 3,5 position, *J* = 6.6), 5.05 (d, 6H, $ArCH_2$, 3,4,5 position, *J* = 5.5), 6.75 (d, 2H, ArH, *meta* to $ArOCH_2$, 4 position, *J* = 8.6), 6.89 (d, 4H, ArH, *meta* to $ArOCH_2$, 3,5 position, *J* = 8.6), 7.22 (d, 2H, ArH, *ortho* to $ArOCH_2$, 4 position, *J* = 8.4), 7.32 (d, 4H, ArH, *ortho* to $ArOCH_2$, 3,5 position, *J* = 8.4), 7.54 (s, 2H, ArH, *ortho* to NO_2); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.3 (CH_3), 22.9 (CH_3CH_2), 26.3 ($CH_2CH_2CH_2O$), 29.5-29.9 ($CH_3CH_2CH_2(CH_2)_6$, CH_2CH_2O), 32.1 ($CH_3CH_2CH_2$), 68.2 (CH_2O, 3,4,5 position), 71.5 ($ArCH_2OAr$, 3,5 position), 75.2 ($ArCH_2OAr$, 4 position), 103.4 (*ortho* to NO_2), 114.5 (*meta* to CH_2OAr, 4 position), 114.7 (*meta* to CH_2OAr, 3,5 position), 127.9 (*ortho* to CH_2OAr, 3,5 position), 128.9 (*ortho* to CH_2OAr, 4 position), 130.5 (*ipso* to CH_2OAr, 3,4,5 position), 142.9 (*para* to NO_2), 144.0 (*ipso* to NO_2), 152.7 (*meta* to NO_2), 159.3 (*para* to CH_2OAr, 3,4,5 position).

3,4,5-Tris-(4-dodecyloxy-benzyloxy)-1-aminobenzene (26). Compound **25** (2 g, 2 mmol), $NH_2NH_2 \cdot H_2O$ (0.5 mL, 10 mmol) and graphite (1 g) were heated in refluxing EtOH-THF mixture (25 mL, 4:1) for 24 h under Ar. The reaction mixture was cooled to room temperature diluted with CH_2Cl_2 (25 mL). Graphite was filtered through diatomaceous earth (Celite 545) and washed several times with CH_2Cl_2. The colorless organic phase was concentrated and precipitated in MeOH twice to yield 1.58 g (82%) of **26** as a white powder. Purity (HPLC): 99+%; TLC (EtOAc/hexane = 3/7): $R_f = 0.24$; m.p. 82-84 °C (ref. [8]): 84-86 °C); ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (t, 9H, CH_3, J = 6.8 Hz), 1.27-1.34 (overlapped m, 48H, $CH_3(CH_2)_8$), 1.42-1.47 (m, 6H, $CH_2(CH_2)_2O$), 1.76-1.80 (m, 6H, CH_2CH_2O), 3.46 (s, 2H, NH_2), 3.90-3.97 (overlapped t, 6H, CH_2OAr, 3,4,5 position), 4.85 (s, 2H, $ArCH_2$, 4 position), 4.96 (s, 4H, $ArCH_2$, 3,5 position), 5.98 (s, 2H, ArH, *ortho* to NH_2), 6.76 (d, 2H, ArH, *meta* to $ArOCH_2$, 4 position, J = 8.6), 6.88 (d, 4H, ArH, *meta* to $ArOCH_2$, 3,5 position, J = 8.7), 7.29 (overlapped d, 6H, ArH, *ortho* to $ArOCH_2$, 3,4,5 position); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.3 (CH_3), 22.9 (CH_3CH_2), 26.3 ($CH_2CH_2CH_2O$), 29.5-29.9 ($CH_3CH_2CH_2(CH_2)_6$, CH_2CH_2O), 32.1 ($CH_3CH_2CH_2$), 68.2 (CH_2O, 3,4,5 position), 71.2 ($ArCH_2OAr$, 3,5 position), 75.2 ($ArCH_2OAr$, 4 position), 96.0 (*ortho* to NH_2), 114.2 (*meta* to CH_2OAr, 4 position), 114.6 (*meta* to CH_2OAr, 3,5 position), 129.2 (*para* to NH_2), 129.4 (*ortho* to CH_2OAr, 3,5 position), 130.5 (*ortho* to CH_2OAr, 4 position), 131.6 (*ipso* to CH_2OAr, 3,4,5 position), 142.8 (*ipso* to NH_2), 153.8 (*meta* to NH_2), 159.0 (*para* to CH_2OAr, 3,4,5 position).

3,4,5-Tris-(4-dodecyloxy-benzyloxy)-*N*-[3,4,5-tris-(4-dodecyloxy-benzyloxy) phenyl)] benzamide (27). Into a stirred solution of **21** (500 mg, 0.50 mmol) and CDMT (97 mg,

0.55 mmol) in dry THF (10 mL), N-methylmorpholine (0.08 mL, 0.75 mmol) was added under Ar. The solution was stirred at room temperature for 1 h. Compound **26** (483 mg, 0.50 mmol) was added and the resulting slurry was stirred for another 4 h. The slurry was diluted with CH_2Cl_2 (10 mL) and poured into MeOH (80 mL). The precipitate was collected by filtration and dried. The obtained crude product was purified by column chromatography (silica gel, EtOAc/hexane 3/7) and precipitated in cold MeOH to yield 680 mg (70%) of **27** as a white powder. Purity (HPLC): 99+%; thermal transitions and the corresponding enthalpy changes are summarized in Table 1; TLC (EtOAc/hexane = 1/9): R_f = 0.72; ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C, TMS): δ = 0.88 (overlapped t, 18H, CH_3, *J* = 6.5 Hz), 1.26 (overlapped m, 96H, $(CH_2)_8$), 1.45 (m, 12H, $CH_2(CH_2)_2O$), 1.77-1.79 (overlapped m, 12H, CH_2CH_2O), 3.90-3.95 (overlapped t, 12H, CH_2OAr), 4.90 (s, 2H, $ArCH_2$, 4 position), 5.02 (d, 10H, $ArCH_2$, 3,5 and 3,4,5 position, *J* = 7.9), 6.77 (d, 4H, ArH, *meta* to $ArOCH_2$, 4 position, *J* = 8.5), 6.88 (dd, 8H, ArH, *meta* to $ArOCH_2$, 3,5 position, *J* = 2.0, 8.6), 6.99 (s, 2H, *ortho* to NHCO), 7.08 (s, 2H, *ortho* to CONH), 7.25-7.33 (m, 12H, ArH, *ortho* to $ArOCH_2$, 3,4,5 position), 7.60 (s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$, 30^{0}C, TMS): δ = 14.3, 22.9, 26.3, 29.5-29.9, 32.1, 68.1, 68.2, 71.2, 71.5, 75.0, 100.2, 107.1, 114.2-114.6, 128.6-129.5, 130.0-130.8, 134.0, 135.3, 141.7, 153.1, 153.2, 159.0-159.3, 165.6 (CONH); MALDI-TOF *m/z*: 1961.61 ($[M+Na]^+$, calculated 1962.86), 1977.85 ($[M+K]^+$, calculated 1978.97).



Reagents and conditions: i) K_2CO_3, DMF, 70 °C, 6 h; ii) $LiAlH_4$, THF, 0 °C-r.t. 2 h; iii) $SOCl_2$, CH_2Cl_2, DMF (catalytic), 20 °C, 1/2 h; iv) K_2CO_3, DMF, 70 °C, 12 h; v) KOH, EtOH (95%), THF, reflux, 2 h; vi) THF, H_3O^+; vii) DCC, DPTS, α,α,α-trifluorotoluene, 50 °C, 6 h.

Scheme 7 (supporting). Synthesis of (4-3,4,5)12G1-(4-3,4,5)12F8G1-BzA (**33**).

Methyl-4-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heptadecafluoro dodecyloxy) benzoate (28): To a thoroughly degassed suspension of anhydrous K_2CO_3 (8.3 g, 60 mmole) in DMF (60 mL) was added methyl-4-hydroxybenzoate, **16** (2.28 g, 15 mmol) and to the reaction mixture heated at 70 °C was added 12-bromo-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro dodecane (8.33 g, 15 mmol) under Ar. After stirring 12 h at 70 °C, the reaction mixture was poured into a stirring ice/water mixture (200 mL). The pale white granular solid was filtered and washed with H_2O. The crude product was passed through a short column of basic Al_2O_3 using CH_2Cl_2 as eluent. Recrystallization from acetone yielded 8.5 g (90%) of white sheet-like crystals. Purity (HPLC): 99+%; m.p. 72-73 °C; TLC (EtOAc/hexane = 3/7): R_f = 0.68; ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C, TMS): δ = 1.82-1.92 (overlapped m, 4H, $CF_2CH_2(CH_2)_2$), 2.17 (m, 2H, CF_2CH_2), 3.89 (s, 3H, CO_2CH_3), 4.06 (t, 2H, CH_2OAr, *J* = 5.8 Hz), 6.99 (d, 2H, 3,5 position, *J* = 8.9), 7.97 (d, 2H, 2,6 position, *J* = 8.9); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C, TMS): δ = 17.5 ($CF_2CH_2CH_2$), 28.8 (CH_2CH_2O), 30.9 (t, CF_2CH_2, *J* = 22.1 Hz), 52.0 (CH_3), 67.6 (CH_2O), 114.3 (3,5 position), 123.0 (1 position), 131.8 (2,6 position), 162.8 (4 position), 167.0 (CO_2CH_3); ^{19}F NMR (470 MHz, $CDCl_3$, 27 °C, TMS): δ = -81.2 (t, 3F, CF_3), -114.7 (m, 2F, CF_2CH_2), -122.2 (m, 6F, $(CF_2)_3CF_2CH_2$), -123.1 (s, 2F, $CF_3(CF_2)_2CF_2$), -123.8 (s 2F, $CF_3CF_2CF_2$), -126.5 (d, 2F, CF_3CF_2).

4-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Heptadecafluoro dodecyloxy) benzyl alcohol (29): To a stirred suspension of $LiAlH_4$ (0.57 g, 15 mmole) in dry THF (30 mL) at 0 °C was added slowly 2**8** (6.26 g, 10 mmol) in dry THF (20 mL) under Ar over a period of 20 min. After complete addition, the reaction mixture was allowed to warm to 22 °C and stirred for 2 h, after which TLC showed completion. The reaction was

quenched by successive addition of H_2O (0.5 mL), 15% aq. NaOH (0.5 mL), and H_2O (1.5 mL) with continuous stirring until H_2 evolution ceased. The reaction mixture was filtered and the lithium salt was washed with THF. The filtrate was dried over $MgSO_4$ and the solvent was removed in a rotary evaporator. Recrystallization from acetone yielded 5.1 g (85%) of white crystals. Purity (HPLC): 99+%; m.p. 85-86 °C; TLC (EtOAc/hexane = 3/7): R_f = 0.30; ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C, TMS): δ = 1.53 (s, 1H, OH), 1.81-1.90 (m, 4H, $CF_2CH_2(CH_2)_2$), 2.16 (m, 2H, CF_2CH_2), 4.01 (m, 2H, CH_2OAr), 4.62 (d, 2H, $ArCH_2OH$, *J* = 4.3), 6.99 (d, 2H, 3,5 position, *J* = 8.4), 7.29 (d, 2H, 2,6 position, *J* = 8.3); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C, TMS): δ = 17.5 ($CF_2CH_2CH_2$), 28.9 (CH_2CH_2O), 30.9 (t, CF_2CH_2, *J* = 22.5 Hz), 65.3 ($ArCH_2OH$), 67.5 (CH_2O), 114.7 (3,5 position), 128.9 (2,6 position), 133.5 (1 position), 158.7 (4 position); ^{19}F NMR (470 MHz, $CDCl_3$, 27 °C, TMS): δ = -81.2 (t, 3F, CF_3), -114.8 (m, 2F, CF_2CH_2), -122.2 (m, 6F, $(CF_2)_3CF_2CH_2$), -123.3 (s, 2F, $CF_3(CF_2)_2CF_2$), -123.9 (s 2F, $CF_3CF_2CF_2$), -126.6 (d, 2F, CF_3CF_2).

4-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Heptadecafluoro dodecyloxy) benzyl chloride (30): A two-neck round bottom flask equipped with a Teflon-coated magnetic stirrer and an Ar inlet was charged with **29** (4.5 g, 7.5 mmol) in dry CH_2Cl_2 (60 mL), CFC-113 (15 mL) and a catalytic amount of DMF. The reaction flask was flushed with Ar, and cooled in an ice bath at 0°C. Thionyl chloride (0.7 mL, 9 mmol) was added dropwise to the cooled reaction mixture. After complete addition, the reaction mixture was stirred at 22 °C for 30 min. The solvent was removed by vacuum distillation and the residue was dissolved in Et_2O, washed with $NaHCO_3$, once with H_2O, dried over anhydrous $MgSO_4$ and filtered. The solvent was removed on a rotary evaporator and

recrystallized from hexane to yield 4.15 g (90%) of white crystals. Purity (HPLC): 99+%; m.p. 55-56 °C; TLC (EtOAc/hexane = 3/7): R_f = 0.79; ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C, TMS): δ = 1.80-1.90 (m, 4H, $CF_2CH_2(CH_2)_2$), 2.18 (m, 2H, CF_2CH_2), 4.00 (t, 2H, CH_2OAr, *J* = 5.7 Hz), 4.57 (s, 2H, $ArCH_2Cl$), 6.86 (d, 2H, 3,5 position, *J* = 8.6), 7.30 (d, 2H, 2,6 position, *J* = 8.5); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C, TMS): δ = 17.2 ($CF_2CH_2CH_2$), 28.9 (CH_2CH_2O), 30.9 (CF_2CH_2), 46.5 ($ArCH_2Cl$), 67.5 (CH_2O), 114.9 (3,5 position), 130.1 (2,6 position), 130.3 (1 position), 159.0 (4 position); ^{19}F NMR (470 MHz, $CDCl_3$, 27 °C, TMS): δ = -81.3 (t, 3F, CF_3), -114.9 (m, 2F, CF_2CH_2), -122.4 (m, 6F, $(CF_2)_3CF_2CH_2$), -123.3 (s, 2F, $CF_3(CF_2)_2CF_2$), -124.1 (s, 2F, $CF_3CF_2CF_2$), -126.7 (m, 2F, CF_3CF_2).

Methyl 3,4,5-tris-[4-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heptadecafluoro dodecyloxy) benzyloxy] benzoate (31): Compound **31** was synthesized by the same general procedure described for the synthesis of compound **20**. From methyl 3,4,5-trihydroxybenzoate (0.36 g, 2 mmol), K_2CO_3 (1.65 g, 12 mmol) and **30** (3.70 g, 6 mmol) in DMF (20 mL) for 12 h at 70 °C, 2.7 g (70%) of a white solid was obtained after passing through a short column of basic Al_2O_3 using 5% CFC-113-CH_2Cl_2 as eluent followed by recrystallization from acetone. Purity (HPLC): 99+%; TLC (EtOAc/hexane = 3/7): R_f = 0.56; ^{1}H NMR (500 MHz, $CDCl_3$, 27 °C, TMS): δ = 1.81-1.90 (overlapped m, 12H, $CF_2CH_2(CH_2)_2$), 2.12-2.20 (m, 6H, CF_2CH_2), 3.89 (s, 3H, CO_2CH_3), 3.96 (t, 2H, CH_2OAr, 4 position, *J* = 5.4 Hz), 4.01 (t, 4H, CH_2OAr, 3,5 position, *J* = 5.6), 5.00 (s, 2H, $ArCH_2$, 4 position), 5.05 (s, 4H, $ArCH_2$, 3,5 position), 6.75 (d, 2H, ArH, *meta* to $ArOCH_2$, 4 position, *J* = 8.6), 6.89 (d, 4H, ArH, *meta* to $ArOCH_2$, 3,5 position, *J* = 8.6), 7.25 (d, 2H, ArH, *ortho* to $ArOCH_2$, 4 position, *J* = 8.4), 7.35 (d, 4H, ArH, *ortho* to

$ArOCH_2$, 3.5 position, J = 8.6), 7.37 (s, 2H, ArH, *ortho* to CO_2CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 27 °C, TMS): δ = 17.5 ($CF_2CH_2CH_2$), 28.9 (CH_2CH_2O), 30.9 (CF_2CH_2), 52.4 (CO_2CH_3), 67.4 ($ArCH_2OAr$, 3,5 position), 71.3 (CH_2OAr), 74.9 ($ArCH_2OAr$, 4 position), 109.4 (*ortho* to CO_2CH_3), 110.9 (CF_2), 114.3 (*meta* to CH_2OAr, 4 position), 114.7 (*meta* to CH_2OAr, 3,5 position), 125.3 (*ipso* to CO_2CH_3), 129.2 (*ortho* to CH_2OAr, 3,5 position), 129.5 (*ortho* to CH_2OAr, 4 position), 130.1 (*ipso* to CH_2OAr, 4 position), 130.5 (*ipso* to CH_2OAr, 3,5 position), 142.7 (*para* to CO_2CH_3), 152.8 (*meta* to CO_2CH_3), 158.8 (*para* to CH_2OAr, 3,4,5 position), 166.9 ($ArCO_2CH_3$); ^{19}F NMR (470 MHz, $CDCl_3$, 27 °C, TMS): δ = -81.2 (t, 9F, CF_3), -114.9 (m, 6F, CF_2CH_2), -122.3 (m, 18F, $(CF_2)_3CF_2CH_2$), -123.2 (s, 6F, $CF_3(CF_2)_2CF_2$), -123.9 (s, 6F, $CF_3CF_2CF_2$), -126.6 (m, 6F, CF_3CF_2).

3,4,5-Tris-[4-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heptadecafluorododecyloxy) benzyloxy] benzoic acid (32): Compound **32** was synthesized by the basic hydrolysis of **31**. Compound **31** (1.93 g, 1 mmol) was dissolved in a refluxing solution of EtOH (25 mL, 95%) and THF (15 mL). To this mixture was added KOH (0.3 g, dissolved in 5 mL of H_2O). After 2 h of reflux, the reaction mixture was cooled to room temperature and diluted with THF (120 mL). The solution was acidified with glacial CH_3COOH, then with dilute HCl to pH 3. The solution was poured into 400 mL ice water and stirred for 15 min. The precipitated solid was collected by filtration and dried. Recrystallization from acetone yielded 1.67 g (87%) of white powder. Purity (HPLC): 99+%; m.p. 147 °C; TLC (EtOAc/hexane = 3/7): R_f = 0; ^1H NMR (500 MHz, $CDCl_3$, 40 °C, TMS): δ = 1.82-1.91 (overlapped m, 12H, $CF_2CH_2(CH_2)_2$), 2.11-2.21 (m, 6H, CF_2CH_2), 3.97 (t, 2H, CH_2OAr, 4 position, J = 5.6 Hz), 4.02 (t, 4H, CH_2OAr, 3,5 position, J = 5.6), 5.03 (s,

2H, $ArCH_2$, 4 position), 5.06 (s, 4H, $ArCH_2$, 3,5 position), 6.75 (d, 2H, ArH, *meta* to $ArOCH_2$, 4 position, J = 8.7), 6.89 (d, 4H, ArH, *meta* to $ArOCH_2$, 3,5 position, J = 8.6), 7.28 (d, 2H, ArH, *ortho* to $ArOCH_2$, 4 position, J = 8.4), 7.34 (d, 4H, ArH, *ortho* to $ArOCH_2$, 3.5 position, J = 8.6), 7.42 (s, 2H, ArH, *ortho* to CO_2CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 40 °C, TMS): δ = 17.6 ($CF_2CH_2CH_2$), 29.1 (CH_2CH_2O), 30.9 (CF_2CH_2), 67.6 ($ArCH_2OAr$, 3,5 position), 71.5 (CH_2OAr), 75.0 ($ArCH_2OAr$, 4 position), 110.3 (*ortho* to CO_2H), 114.5 (*meta* to CH_2OAr, 4 position), 114.8 (*meta* to CH_2OAr, 3,5 position), 124.0 (*ipso* to CO_2H), 129.3 (*ortho* to CH_2OAr, 3,5 position), 129.6 (*ortho* to CH_2OAr, 4 position), 130.2 (*ipso* to CH_2OAr, 4 position), 130.5 (*ipso* to CH_2OAr, 3,5 position), 143.8 (*para* to CO_2H), 153.0 (*meta* to CO_2H), 159.0 (*para* to CH_2OAr, 4 position), 159.1 (*para* to CH_2OAr, 3,5 position); ^{19}F NMR (470 MHz, $CDCl_3$, 40 °C, TMS): δ = -81.2 (t, 9F, CF_3), -114.9 (m, 6F, CF_2CH_2), -122.2 (m, 18F, $(CF_2)_3CF_2CH_2$), -123.0 (s, 6F, $CF_3(CF_2)_2CF_2$), -123.8 (s, 6F, $CF_3CF_2CF_2$), -126.2 (m, 6F, CF_3CF_2).

3,4,5-Tris-[4-(5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12- heptadecafluoro dodecyloxy) benzyloxy]-*N*-(3,4,5-tris-dodecyloxy-phenyl)-benzamide (33). Compound **33** was synthesized by the same procedure described for the preparation of **10**. From **32** (955 mg, 0.5 mmol), and **26** (482 mg, 0.5 mmol) in α,α,α-trifluorotoluene (20 mL) containing DCC (200 mg, 1 mmol) and DPTS (30 mg, 0.1 mmol), 930 mg (65%) of a white solid was obtained after column chromatography (Silica gel, EtOAc/hexane, 3/7) and precipitation in cold MeOH. Purity (HPLC): 99%; thermal transitions and the corresponding enthalpy changes are summarized in Table 1. TLC (EtOAc/hexane = 3/7): R_f = 0.64; ^1H NMR (500 MHz, $CDCl_3$, 27 °C, TMS): δ = 0.88 (overlapped t, 9H, CH_3), 1.26-1.35 (overlapped m, 48H, $(CH_2)_8$), 1.50 (m, 6H, $CH_2(CH_2)_2O$), 1.77-1.79

(overlapped m, 18H,$CF_2(CH_2)_3$), 1.87 (m, 6H, CH_2CH_2O), 3.92-3.99 (overlapped t, 12H, CH_2OAr), 4.90 (s, 2H, $ArCH_2$, 4 position), 5.01 (overlapped s, 10H, $ArCH_2$, 3,5 and 3,4,5 position), 6.75-6.77 (overlapped d, 4H, ArH, *meta* to $ArOCH_2$, 4 position), 6.88 (d, 8H, ArH, *meta* to $ArOCH_2$, 3,5 position, J = 8.6 Hz), 7.00 (s, 2H, *ortho* to NHCO), 7.10 (s, 2H, *ortho* to CONH), 7.30 (overlapped d, 4H, ArH, *ortho* to $ArOCH_2$, 4 position), 7.31-7.33 (dd, 8H, ArH, *ortho* to $ArOCH_2$, 3,5 position, J = 2.1, 6.5), 7.58 (s, 1H, NH); ^{19}F NMR (470 MHz, $CDCl_3$, 27 °C, TMS): δ = -81.2 (t, 9F, CF_3), -114.9 (m, 6F, CF_2CH_2), -122.3 (m, 18F, $(CF_2)_3CF_2CH_2$), -123.9 (s, 6F, $CF_3(CF_2)_2CF_2$), -124.1 (s, 6F, $CF_3CF_2CF_2$), -126.7 (m, 6F, CF_3CF_2); ^{13}C NMR (125 MHz, $CDCl_3$, 30^0C, TMS): δ = 14.3, 17.5, 22.9, 26.3, 28.9, 29.5-29.9, 30.7, 30.9, 32.1, 67.4, 68.3, 71.3, 71.6, 75.1, 100.5, 107.3, 114.3-114.7, 129.0-129.6, 130.0, 130.5, 134.0, 135.6, 141.9, 153.3, 158.9-159.2, 165.5 (CONH); MALDI-TOF *m/z*: 2855.43 (M^+, calculated exact mass 2855.95), 2877.22 ($[M+Na]^+$, calculated 2878.94), 2893.62 ($[M+K]^+$, calculated 2895.05).

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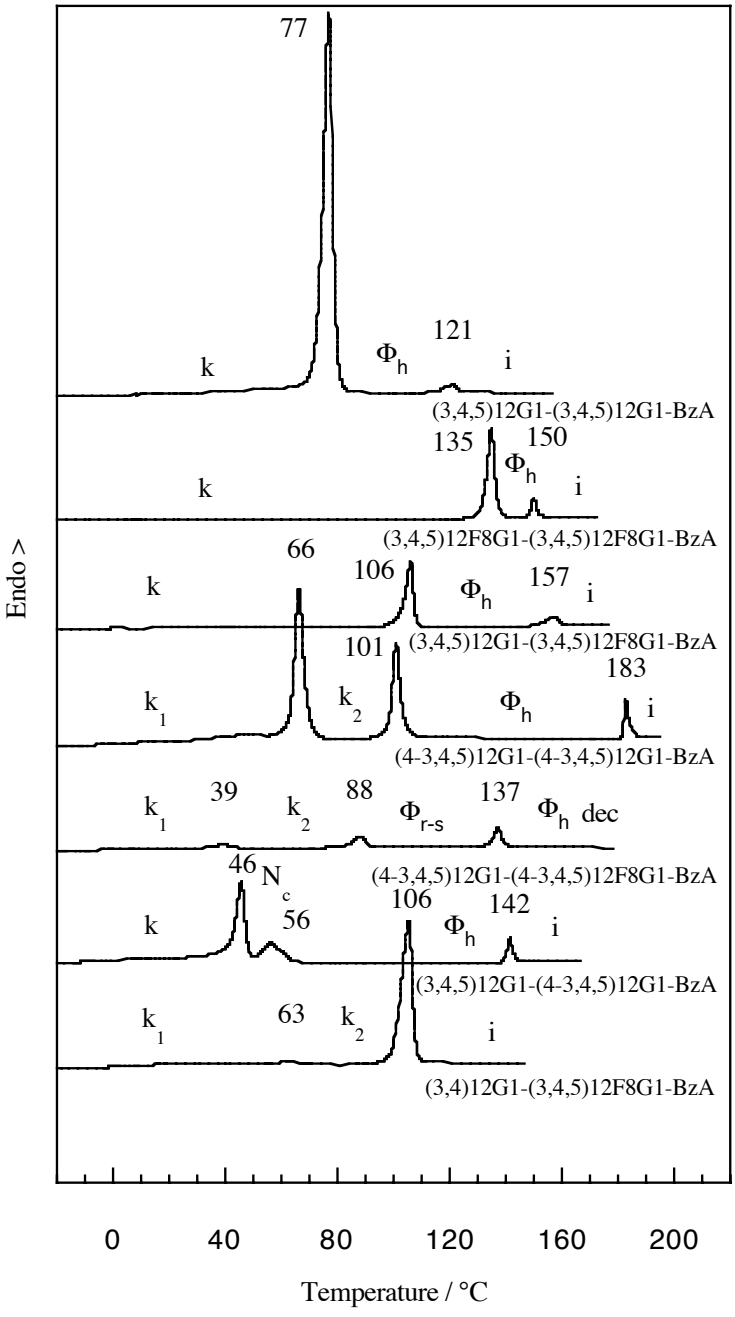

Figure 1 (supporting). DSC traces (first heating cycle, 10 °C/min) of twin-dendritic benzamides and Janus-dendritic benzamides.

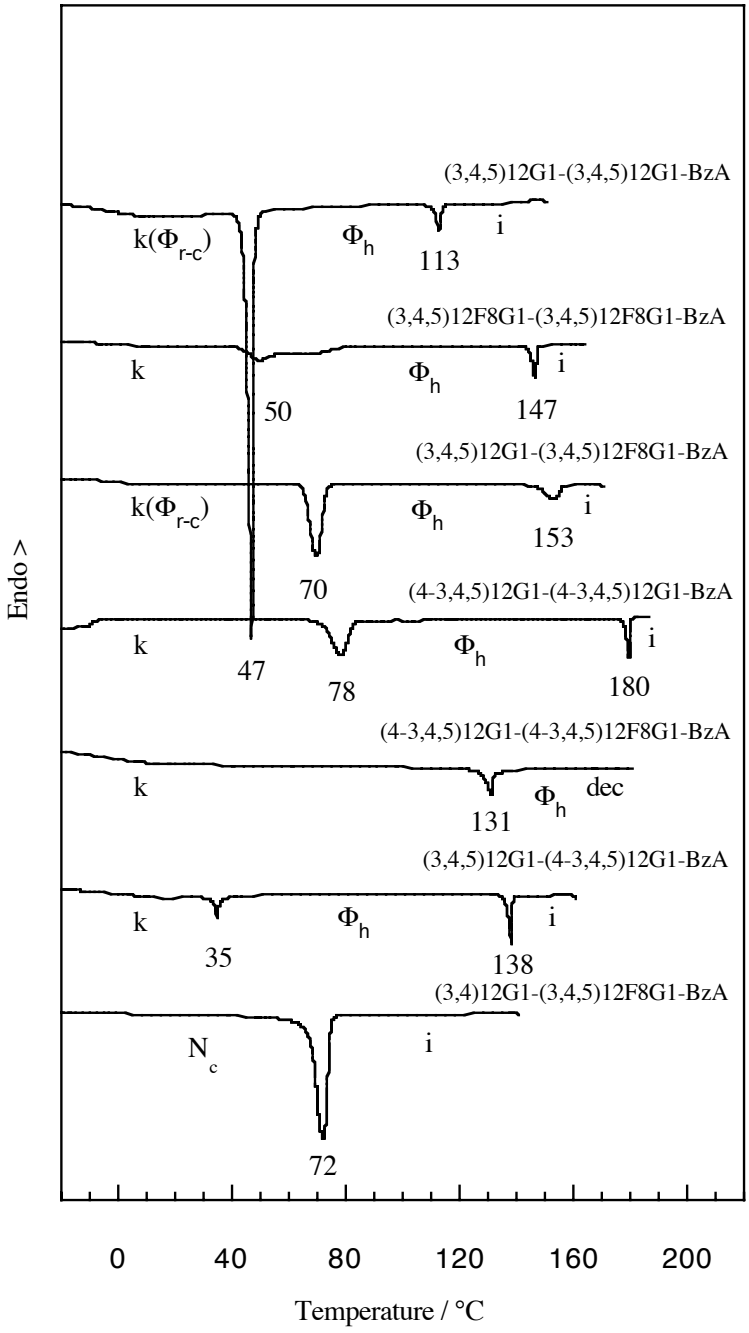

Figure 2 (supporting). DSC traces (first cooling cycle, 10 °C/min) of twin-dendritic benzamides and Janus-dendritic benzamides.

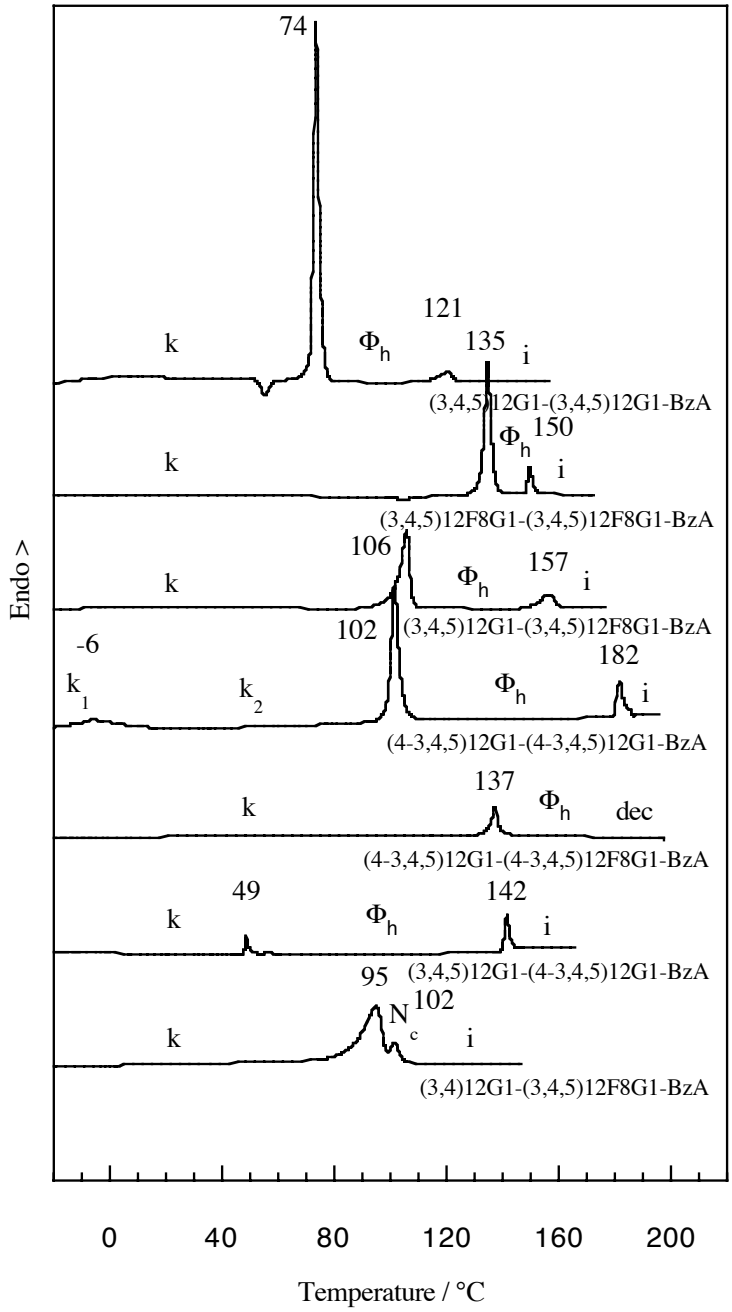

Figure 3 (supporting). DSC traces (second heating cycle, 10 °C/min) of twin-dendritic benzamides and Janus-dendritic benzamides.

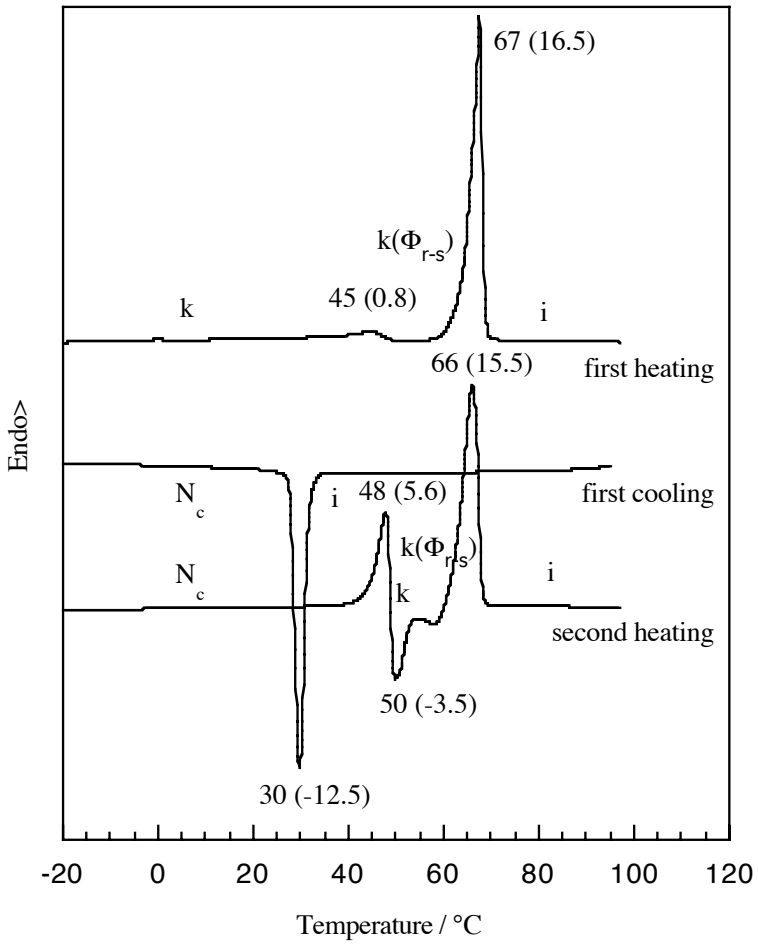

Figure 4 (supporting). DSC traces (5 °C/min) of -NCH_3 derivative (**11a**) of the Janus-dendritic benzamide **(3,4,5)12G1-(3,4,5)12F8G1-BzA**. The enthalpy changes (kcal/mol) associated with the phase transitions are shown in parenthesis. *d*-spacings [Å] with indices for the *p2mm* simple rectangular columnar lattice ($\Phi_{r\text{-}s}$) are: 31.5 (10), 26.1 (02), 17.6 (03) and 15.7 (20) as observed by XRD. Lattice dimension for $\Phi_{r\text{-}s}$: a = 31.4 Å, b = 52.7 Å (T = 60 °C).