

**Increasing 3D Supramolecular Order by Decreasing Molecular Order. A
Comparative Study of Helical Assemblies of Dendronized Non-Chlorinated and
Tetrachlorinated Perylene Bisimides**

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1. Materials

Zinc acetate dihydrate ($\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$), quinoline, carbon tetrabromide (CBr_4), sodium azide (NaN_3), triphenylphosphine (PPh_3) (all from Acros), lithium aluminium hydride (LiAlH_4), diisopropyl azodicarboxylate (DIAD) (all from Aldrich), pyridine, DMF, EtOH (all from Fisher, ACS reagents) and potassium carbonate (K_2CO_3) (from Alfa Aesar), were used as received. Dichloromethane (CH_2Cl_2) (from Fisher, ACS reagent) was dried over CaH_2 and freshly distilled before use. THF (from Fisher, ACS reagent) was refluxed over sodium benzophenone ketyl until the solution turned purple and then was freshly distilled before use.

2. Techniques

Solution NMR

^1H 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 a Perkin-Elmer Series 10 high pressure liquid chromatograph with an LC-100 column oven, Nelson Analytical 900 series integrator data station and two Perkin-Elmer PL gel column 5×10^2 and 1×10^4 Å. THF was used as solvent with a UV detector.

Differential Scanning Calorimetry

Thermal transitions were measured on TA instrument 2920 modulated and Q100 differential scanning calorimeter (DSC) integrated with a refrigerated cooling system (RCS). The heating and cooling rates were 1 or 10 °C/min. The transition temperatures were measured as the maxima and minima of their endothermic and exothermic peaks. Indium and sapphire were used as standards for calibration. An Olympus BX-51 optical polarized microscope (100× magnification) equipped with a Mettler FP 82HT hot stage and Mettler 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 $^{\circ}\text{C}$ 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 $\text{Cu-K}_{\alpha 1}$ radiation ($\lambda = 1.542 \text{ \AA}$) from a Bruker-Nonius FR-591 rotating anode X-ray source equipped with a $0.2 \times 0.2 \text{ mm}^2$ 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 $0.3 \times 0.3 \text{ mm}^2$ 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: $\pm 0.1 \text{ }^{\circ}\text{C}$, temperature range from $-120 \text{ }^{\circ}\text{C}$ to $270 \text{ }^{\circ}\text{C}$). 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.^{S1} The powdered sample ($\sim 10 \text{ mg}$) was heated inside the extrusion device. After slow cooling, the fiber was extruded in the liquid crystal phase and cooled to $23 \text{ }^{\circ}\text{C}$. 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).^{S2} Molecular models were built and visualized using Materials Studio (Accelrys).

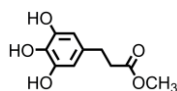
Solid State NMR Experiments

2D ^1H double-quantum (DQ) NMR correlation spectra were recorded with a Bruker Avance III console operating at 850.13 MHz ^1H Larmor frequency using a commercial double resonance probe supporting zirconia rotors with an outer diameter of 2.5 mm. Measurements were performed at 30 kHz MAS spinning frequency using the improved Back-to-Back (BaBa) excitation scheme^{S3,S4} for double quantum excitation and reconversion with 125 kHz rf nutation frequency on the ^1H channel.

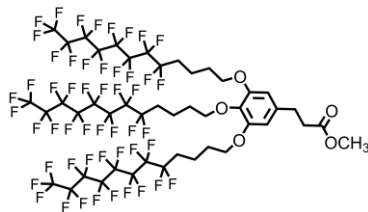
2D $^{13}\text{C}\{^1\text{H}\}$ heteronuclear Lee-Goldburg Cross-Polarization (LGCP) correlation experiments^{S5} were recorded at 18 kHz MAS and 700.23 MHz ^1H Larmor frequency (176.1 MHz ^{13}C Larmor frequency)

using an LGCP contact time of 3 ms and 102 kHz FSLG multi pulse decoupling for line narrowing in the ^1H dimension and SPINAL64 decoupling during ^{13}C acquisition.

3. Synthesis

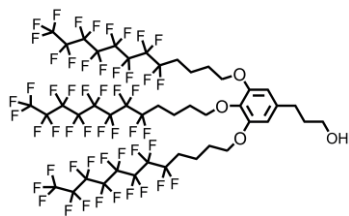


Methyl 3-(3,4,5-trihydroxyphenyl)propanoate (1). This compound was synthesized according to a literature procedure.^{S6}



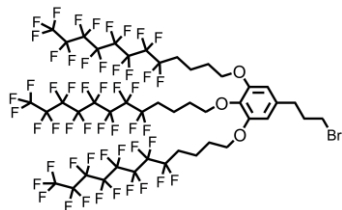
Methyl 3-(3,4,5-tris((1H,1H,2H,2H,3H,3H,4H,4H-perfluorododecyl)oxy)phenyl)propanoate (2).

Into a solution of methyl 3-(3,4,5-trihydroxyphenyl)propanoate (**1**) (0.70 g, 3.30 mmol) in degassed DMF (70 mL) was added 1H,1H,2H,2H,3H,3H,4H,4H-perfluorododecyl bromide (5.50 g, 10.0 mmol) and K_2CO_3 (4.00 g, 29.0 mmol). The reaction mixture was allowed to stir under N_2 at 75 °C for 8 h. The mixture was cooled to room temperature and poured into water. The solid was filtered and dried to give the crude product which was further purified by recrystallization from acetone to give a white solid (4.10 g, 77 %). Purity (HPLC): 99%+. ^1H NMR (500 MHz, CDCl_3), δ (ppm): 6.40 (s, 2H, ArH), 3.99 (t, $^3J = 5.5$ Hz, 4H, CH_2OAr , 3- and 5-positions), 3.92 (t, $^3J = 5.5$ Hz, 2H, CH_2OAr , 4-position), 3.67 (s, 3H, CO_2CH_3), 2.87 (t, $^3J = 7.4$ Hz, 2H, $\text{ArCH}_2\text{CH}_2\text{CO}_2\text{CH}_3$), 2.61 (t, $^3J = 7.8$ Hz, 2H, $\text{ArCH}_2\text{CH}_2\text{CO}_2\text{CH}_3$), 2.22–2.06 (m, 6H, $3(\text{C}_8\text{F}_{17})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OAr}$), 1.93–1.76 (m, 12H, $3(\text{C}_8\text{F}_{17})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OAr}$). ^{13}C NMR (126 MHz, CDCl_3), δ (ppm): 173.4 ($\text{C}=\text{O}$), 152.9 (ArC (C3,5)), 136.5 (ArC (C4)), 136.4 (ArC (C1)), weak, broad CF multiplets appear at 128–110, 107.0 (ArC (C2,6)), 72.7 (CH_2OAr , 4-position), 68.5 (CH_2OAr , 3- and 5-positions), 51.8 (CO_2CH_3), 36.0 ($\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2(\text{C}_8\text{F}_{17})$), 31.4 ($\text{CH}_2\text{CO}_2\text{CH}_3$), 29.9 (CH_2Ar), 29.0 ($\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2(\text{C}_8\text{F}_{17})$), 17.5 ($\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2(\text{C}_8\text{F}_{17})$). MALDI-TOF (m/z): calc. for $[\text{C}_{46}\text{H}_{33}\text{F}_{51}\text{NaO}_5]^+$: 1657.14; found: 1656.36 $[\text{M}+\text{Na}]^+$.



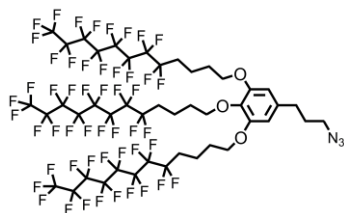
Methyl 3-(3,4,5-tris((1H,1H,2H,2H,3H,3H,4H,4H-perfluorododecyl)oxy)phenyl)propan-1-ol (3).

Into a suspension of LiAlH_4 (0.20 g, 5.27 mmol) in dry THF (20 mL) was added dropwise a solution of ester **2** (3.00 g, 1.84 mmol) in dry THF (30 mL) at 0 °C. The reaction mixture was allowed to stir at 25 °C for 90 min. The reaction mixture was quenched by successive dropwise addition of H_2O (0.2 mL), aqueous NaOH solution (15% w/w, 0.2 mL) and H_2O (0.6 mL). The granular salts were filtered through Celite and washed with generous rinsings of THF. The filtrate was evaporated *in vacuo* and the resultant solid recrystallized from acetone to obtain the product as a white solid (2.50 g, 85%). Purity (HPLC): 99%+. ^1H NMR (500 MHz, CDCl_3), δ (ppm): 6.37 (s, 2H, ArH), 3.95 (t, $^3J = 6.0$ Hz, 4H, CH_2OAr , 3- and 5-positions), 3.89 (t, $^3J = 6.0$ Hz, 2H, CH_2OAr , 4-position), 3.67 (s, 1H, OH), 3.62 (m, 2H, $\text{ArCH}_2\text{CH}_2\text{CH}_2\text{OH}$), 2.59 (t, $^3J = 7.3$ Hz, 2H, $\text{ArCH}_2\text{CH}_2\text{CH}_2\text{OH}$), 2.21–1.98 (m, 6H, $3(\text{C}_8\text{F}_{17})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OAr}$), 1.91–1.72 (m, 14H, $3(\text{C}_8\text{F}_{17})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OAr}$ and $\text{ArCH}_2\text{CH}_2\text{CH}_2\text{OH}$). ^{13}C NMR (126 MHz, CDCl_3), δ (ppm): 152.8 (ArC (C3,5)), 137.9 (ArC (C4)), 136.0 (ArC (C1)), weak, broad CF multiplets appear at 128–110, 107.1 (ArC (C2,6)), 72.6 (CH_2OAr , 4-position), 68.4 (CH_2OAr , 3- and 5-positions), 62.0 (CH_2OH), 34.4 ($\text{CH}_2\text{CH}_2\text{OH}$), 32.5 ($\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2(\text{C}_8\text{F}_{17})$), 29.8 (CH_2Ar), 29.0 ($\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2(\text{C}_8\text{F}_{17})$), 17.4 ($\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2(\text{C}_8\text{F}_{17})$). MALDI-TOF (m/z): calc. for $[\text{C}_{45}\text{H}_{34}\text{F}_{51}\text{O}_4]^+$: 1607.17; found: 1608.60 $[\text{M}+\text{H}]^+$.

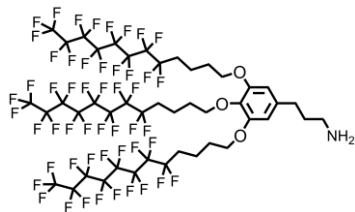


5-(3-Bromopropyl)-1,2,3-tris((1H,1H,2H,2H,3H,3H,4H,4H-perfluorododecyl)oxy)benzene (4). Into a solution of alcohol **3** (2.20 g, 1.37 mmol) and CBr_4 (0.68 g, 2.05 mmol) in dry CH_2Cl_2 (40 mL) was added slowly a solution of PPh_3 (0.55 g, 2.05 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was allowed to stir at 25 °C for 3 h under N_2 . The mixture was concentrated and added to cold MeOH to precipitate the product, which was isolated by vacuum filtration as a white solid (1.90 g, 84%) which was used in the next step without further purification. Purity (HPLC): 99%+. ^1H NMR (500 MHz, CDCl_3), δ (ppm): 6.39 (s, 2H, ArH), 3.99 (t, $^3J = 5.4$ Hz, 4H, CH_2OAr , 3- and 5-positions), 3.92 (t, $^3J = 5.4$ Hz, 2H, CH_2OAr , 4-position), 3.38 (t, $^3J = 6.4$ Hz, 2H, $\text{ArCH}_2\text{CH}_2\text{CH}_2\text{Br}$), 2.69 (t, $^3J = 7.2$ Hz, 2H,

ArCH₂CH₂CH₂Br), 2.22–2.05 (m, 6H, 3(C₈F₁₇)CH₂CH₂CH₂CH₂OAr), 1.93–1.75 (m, 14H, 3(C₈F₁₇)CH₂CH₂CH₂CH₂OAr and ArCH₂CH₂CH₂Br). ¹³C NMR (126 MHz, CDCl₃), δ (ppm): 152.9 (ArC (C3,5)), 136.4 (ArC (C4)), 136.3 (ArC (C1)), weak, broad CF multiplets appear at 128–110, 107.3 (ArC (C2,6)), 72.7 (CH₂OAr, 4-position), 68.5 (CH₂OAr, 3- and 5-positions), 34.3 (CH₂Ar), 34.2 (CH₂CH₂Br), 33.2 (CH₂Br), 30.8 (OCH₂CH₂CH₂CH₂(C₈F₁₇)), 29.0 (OCH₂CH₂CH₂CH₂(C₈F₁₇)), 17.5 (OCH₂CH₂CH₂CH₂(C₈F₁₇)). MALDI-TOF (m/z): calc. for [C₄₅H₃₃BrF₅₁O₃]⁺: 1669.08; found: 1670.68 [M+H]⁺.

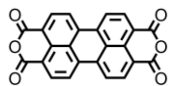


5-(3-Azidopropyl)-1,2,3-tris((1H,1H,2H,2H,3H,3H,4H,4H-perfluorododecyl)oxy)benzene (5). Into a solution of bromide **4** (1.50 g, 0.90 mmol) in dry DMF (10 mL) was added NaN₃ (0.30 g, 4.62 mmol). The reaction mixture was stirred at 85 °C for 16 h. The reaction mixture was cooled to room temperature whereupon it was filtered. The filtrate was collected and the solvent was evaporated *in vacuo* to give the product as an off white-solid (1.10 g, 75%) which was used in the next step without further purification. Purity (HPLC): 99%+. ¹H NMR (500 MHz, CDCl₃), δ (ppm): 6.32 (s, 2H, ArH), 3.92 (m, 4H, CH₂OAr, 3- and 5-positions), 3.86 (m, 2H, CH₂OAr, 4-position), 3.21 (t, ³J = 7.0 Hz, 2H, ArCH₂CH₂CH₂N₃), 2.55 (t, ³J = 7.0 Hz, 2H, ArCH₂CH₂CH₂N₃), 2.19–1.99 (m, 6H, 3(C₈F₁₇)CH₂CH₂CH₂CH₂OAr), 1.87–1.66 (m, 14H, 3(C₈F₁₇)CH₂CH₂CH₂CH₂OAr and ArCH₂CH₂CH₂N₃). ¹³C NMR (126 MHz, CDCl₃), δ (ppm): 152.8 (ArC (C3,5)), 136.6 (ArC (C4)), 136.1 (ArC (C1)), weak, broad CF multiplets appear at 128–110, 107.0 (ArC (C2,6)), 72.5 (CH₂OAr, 4-position), 68.3 (CH₂OAr, 3- and 5-positions), 50.6 (CH₂N₃), 33.0 (CH₂Ar), 30.6 (CH₂CH₂N₃), 30.5 (OCH₂CH₂CH₂CH₂(C₈F₁₇)), 28.9 (OCH₂CH₂CH₂CH₂(C₈F₁₇)), 17.3 (OCH₂CH₂CH₂CH₂(C₈F₁₇)). MALDI-TOF (m/z): calc. for [C₄₅H₃₃F₅₁NO₃]⁺: 1604.17; found: 1604.40 [M+H–N₂]⁺.

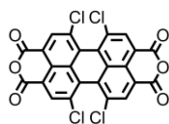


Methyl 3-(3,4,5-tris((1H,1H,2H,2H,3H,3H,4H,4H-perfluorododecyl)oxy)phenyl)propan-1-amine (6). Into a suspension of LiAlH₄ (0.20 g, 5.27 mmol) in dry THF (10 mL) was added slowly a solution of azide **5** (0.80 g, 0.50 mmol) in dry THF (15 mL) at 0 °C. The reaction mixture was allowed to stir at 25 °C for 3 h. The reaction mixture was quenched by successive dropwise addition of H₂O (0.2 mL),

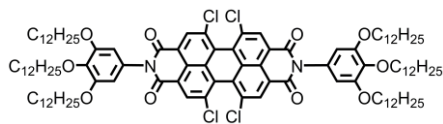
aqueous NaOH solution (15% w/w, 0.2 mL) and H₂O (0.6 mL). The granular salts were filtered through Celite and washed with generous rinsings of THF. The filtrate was evaporated *in vacuo* to obtain the product as an off-white solid which was used in the next step without further purification. (0.69 g, 88%). Purity (HPLC): 99%+. ¹H NMR (500 MHz, CDCl₃), δ (ppm): 6.39 (s, 2H, ArH), 4.00 (t, ³J = 5.4 Hz, 4H, CH₂OAr, 3- and 5-positions), 3.93 (t, ³J = 5.7 Hz, 2H, CH₂OAr, 4-position), 2.73 (t, ³J = 6.9 Hz, 2H, ArCH₂CH₂CH₂NH₂), 2.57 (t, ³J = 7.5 Hz, 2H, ArCH₂CH₂CH₂NH₂), 2.23–2.05 (m, 6H, 3(C₈F₁₇)CH₂CH₂CH₂CH₂OAr), 1.94–1.77 (m, 14H, 3(C₈F₁₇)CH₂CH₂CH₂CH₂OAr), 1.75 (t, 2H, ArCH₂CH₂CH₂NH₂), 1.43 (s, 2H, NH₂). ¹³C NMR (126 MHz, CDCl₃), δ (ppm): 152.8 (ArC (C3,5)), 138.1 (ArC (C4)), 136.1 (ArC (C1)), weak, broad CF multiplets appear at 128–110, 107.1 (ArC (C2,6)), 72.7 (CH₂OAr, 4-position), 68.5 (CH₂OAr, 3- and 5-positions), 41.9 (CH₂NH₂), 33.7 (CH₂Ar), 29.9 (CH₂CH₂NH₂), 29.0 (OCH₂CH₂CH₂CH₂(C₈F₁₇)), 29.0 (OCH₂CH₂CH₂CH₂(C₈F₁₇)), 17.5 (OCH₂CH₂CH₂CH₂(C₈F₁₇)). MALDI-TOF (m/z): calc. for [C₄₅H₃₅F₅₁NO₃]⁺: 1606.18; found: 1606.19 [M+H]⁺.



Perylene-3,4,9,10-tetracarboxylic dianhydride (7a). This compound was purchased from Aldrich and used as received.

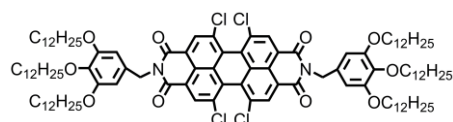


2,5,8,11-Tetrachloroperylene-tetracarboxylic acid bisanhydride (7b). This compound was synthesized according to a modified literature procedure.^{S7} A mixture of perylene-3,4,9,10-tetracarboxylic dianhydride (**7a**) (5.00 g, 12.7 mmol) and iodine (0.54g, 2.12 mmol) in chlorosulfonic acid (20 mL) was stirred at 65 °C for 20 h. The hot solution was filtered to remove insoluble unreacted starting materials and insoluble by-products. The filtrate was added dropwise into ice cold water with stirring and the resulting precipitate was filtered, washed generously with water and dried in an oven. In contrast to the red solid starting material, the product was an orange solid (6.35 g, 94%) which exhibited moderate solubility in THF and chloroform. The product was used in the next step without further purification. ¹H NMR (500 MHz, CDCl₃), δ (ppm): 8.77 (s, 4H, Per-H).



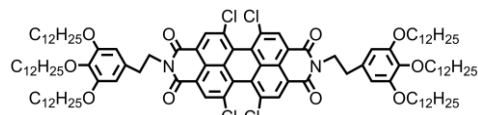
(3,4,5)12G1-0-Cl₄PBI (8a). A suspension of 2,5,8,11-tetrachloroperylene-tetracarboxylic acid bisanhydride (**7b**) (0.33 g, 0.62 mmol), 3,4,5-tris(dodecyl-1-oxy)phenylamine (**12a**) (0.80 g, 1.24 mmol)

and $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.16 g, 0.95 mmol) in quinoline (20 mL) was stirred at 180 °C under N_2 for 4 h. The reaction mixture was cooled to room temperature and poured into HCl (1M, 80 mL). The resulting precipitate was filtered, washed with water (50 mL) and MeOH (50 mL) and dried. The crude product was purified by column chromatography (SiO_2 , CH_2Cl_2). The resulting red solid was dissolved in THF and precipitated by the addition of MeOH. The precipitate was collected by vacuum filtration, washed with MeOH and dried *in vacuo* to afford product as a red solid (0.95 g, 69%). Purity (HPLC): 99%+. TLC (SiO_2 , CH_2Cl_2): R_f = 0.95. ^1H NMR (500 MHz, CDCl_3), δ (ppm): 8.96 (s, 4H, ArH of PBI core), 6.52 (s, 4H, ArH *ortho* to OAlk), 4.09 (t, 3J = 6.8 Hz, 8H, 4Alk $\text{CH}_2\text{CH}_2\text{CH}_2\text{OAr}$), 3.92 (t, 3J = 6.8 Hz, 4H, 2Alk $\text{CH}_2\text{CH}_2\text{CH}_2\text{OAr}$), 1.85–1.81 (m, 12H, 6Alk $\text{CH}_2\text{CH}_2\text{CH}_2\text{OAr}$), 1.46 (m, 12H, 6Alk $\text{CH}_2\text{CH}_2\text{CH}_2\text{OAr}$), 1.29 (m, 96H, 6 $\text{CH}_3(\text{CH}_2)_8$), 0.88 (t, 3J = 6.3 Hz, 18H, 6 CH_3). ^{13}C NMR (126 MHz, CDCl_3), δ (ppm): 163.2 (C=O) 153.5 (ArC (C3)), 138.5 (ArC (C4)), 135.0 (ArC (C1)), signals at 133.1, 132.7, 132.2, 131.2, 131.0 and 130.0 correspond to perylene carbons, 108.9 (ArC (C2)), 93.8 (CH_2OAr , 4-position), 69.6 (CH_2OAr , 3- and 5-positions), 32.4 ($\text{CH}_3\text{CH}_2\text{CH}_2$), 30.9 ($\text{CH}_2\text{CH}_2\text{OAr}$), 30.4–30.1 ($\text{CH}_3(\text{CH}_2)_3(\text{CH}_2)_5$), 30.0 ($\text{CH}_3(\text{CH}_2)_2\text{CH}_2$), 26.5 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{OAr}$), 23.3 (CH_2CH_3), 14.5 (CH_3). MALDI-TOF (m/z): calc. for $[\text{C}_{108}\text{H}_{158}\text{Cl}_4\text{NaN}_2\text{O}_{10}]^+$: 1806.09; found: 1812.24 $[\text{M}+\text{Na}]^+$.

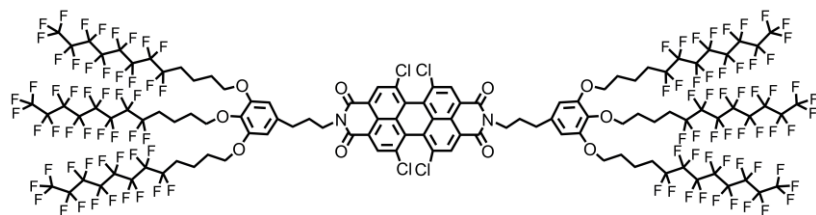


(3,4,5)12G1-1-Cl₄PBI (8b). A suspension of 2,5,8,11-tetrachloroperylene-tetracarboxylic acid bisanhydride (**7b**) (0.48 g, 0.90 mmol), 3,4,5-tris(dodecyl-1-oxy)benzylamine (**12b**) (1.20 g, 1.82 mmol) and $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.16 g, 0.95 mmol) in quinoline (20 mL) was stirred at 180 °C under N_2 for 6 h. The reaction mixture was cooled to room temperature and poured into HCl (1M, 80 mL). The resulting precipitate was filtered, washed with water (50 mL) and MeOH (50 mL) and dried. The crude product was purified by column chromatography (SiO_2 , CH_2Cl_2). The resulting red solid was dissolved in THF and precipitated by the addition of MeOH. The precipitate was collected by vacuum filtration, washed with MeOH and dried *in vacuo* to afford product as a red solid (1.45 g, 84%). Purity (HPLC): 99%+. TLC (SiO_2 , CH_2Cl_2): R_f = 0.95. ^1H NMR (500 MHz, CDCl_3), δ (ppm): 8.92 (s, 4H, ArH of PBI core), 6.89 (s, 4H, ArH *ortho* to OAlk), 5.31 (s, 4H, NCH_2Ar), 4.02 (t, 3J = 6.8 Hz, 8H, 4Alk $\text{CH}_2\text{CH}_2\text{CH}_2\text{OAr}$), 3.92 (t, 3J = 6.8 Hz, 4H, 2Alk $\text{CH}_2\text{CH}_2\text{CH}_2\text{OAr}$), 1.99–1.81 (m, 12H, 6Alk $\text{CH}_2\text{CH}_2\text{CH}_2\text{OAr}$), 1.49 (m, 12H, 6Alk $\text{CH}_2\text{CH}_2\text{CH}_2\text{OAr}$), 1.29 (m, 96H, 6 $\text{CH}_3(\text{CH}_2)_8$), 0.89 (t, 3J = 6.3 Hz, 18H, 6 CH_3). ^{13}C NMR (126 MHz, CDCl_3), δ (ppm): 163.2 (C=O) 153.4 (ArC (C3)), 138.5 (ArC (C4)), 135.1 (ArC (C1)), signals at 133.1, 132.9, 132.2, 131.1, 131.0 and 129.9 correspond to perylene carbons, 109.0 (ArC (C2)), 93.8 (CH_2OAr , 4-position), 69.7 (CH_2OAr , 3- and 5-positions), 48.3

(CH₂Ar), 32.3 (CH₃CH₂CH₂), 30.9 (CH₂CH₂OAr), 30.3–30.0 (CH₃(CH₂)₃(CH₂)₅), 29.9 (CH₃(CH₃)₂CH₂), 26.5 (CH₂CH₂CH₂OAr), 23.2 (CH₂CH₃), 14.5 (CH₃). MALDI-TOF (m/z): calc. for [C₁₁₀H₁₆₂Cl₄NaN₂O₁₀]⁺: 1834.09; found: 1833.50 [M+Na]⁺.

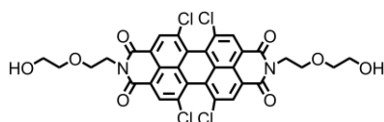


(3,4,5)12G1-2-Cl₄PBI (8c). A suspension of 2,5,8,11-tetrachloroperylene-tetracarboxylic acid bisanhydride (**7b**) (0.30 g, 0.56 mmol), 2-(3,4,5-tris(dodecyl-1-oxy)phenyl)ethylamine (**8c**) (0.80 g, 1.18 mmol) and Zn(OAc)₂·2H₂O (0.16 g, 0.95 mmol) in quinoline (20 mL) was stirred at 180 °C under N₂ for 5 h. The reaction mixture was cooled to room temperature and poured into HCl (1M, 30 mL). The resulting precipitate was filtered, washed with water (20 mL) and MeOH (20 mL) and dried. The crude product was purified by column chromatography (SiO₂, CH₂Cl₂). The resulting red solid was dissolved in CH₂Cl₂ and precipitated by the addition of MeOH. The precipitate was collected by vacuum filtration, washed with MeOH and dried *in vacuo* to afford product as a red solid (0.82 g, 98%). Purity (HPLC): 99%+. TLC (SiO₂, CH₂Cl₂): R_f = 0.90. ¹H NMR (500 MHz, CDCl₃), δ (ppm): 8.92 (s, 4H, ArH of BPI core), 6.55 (s, 2H, ArH *ortho* to OAlk), 4.49 (t, *J* = 5.8 Hz, 4H, ArCH₂CH₂N), 3.91–3.99 (m, 12H, 6AlkCH₂CH₂CH₂OAr), 2.99 (t, *J* = 5.8 Hz, 4H, ArCH₂CH₂N), 1.81 (m, 12H, 6AlkCH₂CH₂CH₂OAr), 1.49 (m, 12H, 6AlkCH₂CH₂CH₂OAr), 1.29 (m, 96H, 6CH₃(CH₂)₈), 0.90 (t, *J* = 6.3 Hz, 18H, 6CH₃). ¹³C NMR (126 MHz, CDCl₃), δ (ppm): 163.3 (C=O), 153.3 (ArC (C3)), 135.0 (ArC (C1)), 132.8 (ArC (C4)), signals at 133.2, 131.0, 132.3, 131.2, 130.7 and 130.0 correspond to perylene carbons, 105.5 (ArC (C2)), 92.9 (CH₂OAr, 4-position), 69.2 (CH₂OAr, 3- and 5-positions), 49.81 (ArCH₂CH₂), 39.82 (ArCH₂CH₂), 32.5 (CH₃CH₂CH₂), 30.9 (CH₂CH₂OAr), 30.4–30.2 (CH₃(CH₂)₃(CH₂)₅), 29.6 (CH₃(CH₃)₂CH₂), 26.7 (CH₂CH₂CH₂OAr), 23.2 (CH₂CH₃), 14.5 (CH₃). MALDI-TOF (m/z): calc. for [C₁₁₂H₁₆₆Cl₄NaN₂O₁₀]⁺: 1862.12; found: 1861.28 [M+Na]⁺.

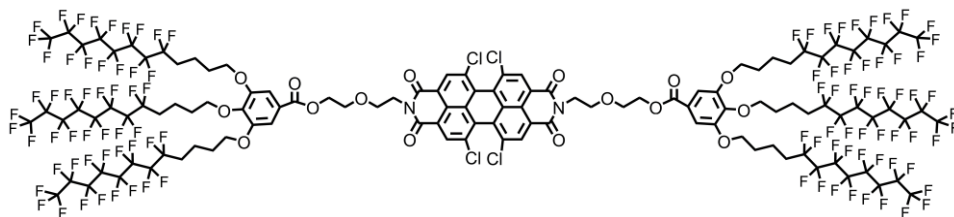


(3,4,5)12F8G1-3-Cl₄PBI (9). A mixture of 2,5,8,11-tetrachloroperylene-tetracarboxylic acid bisanhydride (**7b**) (0.10 g, 0.19 mmol), amine **6** (0.60 g, 0.38 mmol), and Zn(OAc)₂·2H₂O (0.20 g, 0.91 mmol) in quinoline (30.0 mL) was heated at 180 °C for 6 h under N₂. The reaction mixture was allowed to cool to room temperature whereupon it was poured into HCl (1M). The red precipitate was collected by filtration and washed with water and MeOH. The crude product was purified by column chromatography (SiO₂, CH₂Cl₂) to afford the product as a red solid (0.45 g, 64%). Purity (HPLC):

99%+. ^1H NMR (500 MHz, CDCl_3), δ (ppm): 8.65 (s, 4H, Per-*H*), 6.45 (s, 4H, Ar*H*), 4.28 (t, $^3J = 7.7$ Hz, 4H, NCH_2), 4.01 (t, $^3J = 5.5$ Hz, 8H, CH_2OAr , 3- and 5-positions), 3.79 (m, 2H, CH_2OAr , 4-position), 2.73 (t, $^3J = 7.5$ Hz, 4H, ArCH_2), 2.24–2.00 (m, 16H, $6(\text{C}_8\text{F}_{17})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OAr}$ and $2\text{ArCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$), 1.95–1.66 (m, 24H, $6(\text{C}_8\text{F}_{17})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OAr}$). ^{13}C NMR (126 MHz, CDCl_3), δ (ppm): 162.3, 152.6, 136.8, 135.7, 135.4, 132.9, 131.4, 128.6, 123.2, 121.3–107.3 (several broad CF multiplets), 106.5, 72.4, 68.1, 40.7, 33.5, 30.8, 30.6, 30.5, 29.7, 29.6, 28.9, 28.6, 17.3, 17.1. MALDI-TOF (m/z): calc. for $[\text{C}_{114}\text{H}_{68}\text{Cl}_4\text{F}_{102}\text{N}_2\text{NaO}_{10}]^+$: 3725.19; found: 3725.18 $[\text{M}+\text{Na}]^+$.

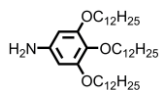


Bis-*N,N'*-(2-(2-hydroxyethoxy)ethyl)-perylene-3,4,9,10-tetracarboxylic diimide (10). A mixture of 2,5,8,11-tetrachloroperylene-tetracarboxylic acid bisanhydride (**7b**) (0.50 g, 0.94 mmol), 2-(2-aminoethoxy)ethanol (**13**) (0.20 g, 1.90 mmol), and $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.10 g, 0.46 mmol) in pyridine (20 mL) was heated at 120 °C for 3 h under N_2 . The reaction mixture was allowed to cool to room temperature whereupon it was poured into HCl (1M). The red precipitate was collected by filtration and washed with water and MeOH to afford the product as a red solid (0.55 g, 83%). Purity (HPLC): 99%+. ^1H NMR (500 MHz, CDCl_3), δ (ppm): 8.69 (s, 4H, Per-*H*), 4.49 (m, 4H, OCH_2), 3.88 (m, 4H, OCH_2), 3.71 (m, 4H, OCH_2), 3.67 (m, 4H, NCH_2). ^{13}C NMR (126 MHz, CDCl_3), δ (ppm): 162.7 ($\text{C}=\text{O}$), 137.5, 135.6, 133.3, 128.9 and 123.2 correspond to perylene carbons, 72.4 ($\text{OCH}_2\text{CH}_2\text{OH}$), 68.4 (NCH_2CH_2), 62.0 (CH_2OH), 40.2 (NCH_2). MALDI-TOF (m/z): calc. for $[\text{C}_{32}\text{H}_{22}\text{Cl}_4\text{N}_2\text{NaO}_8]^+$: 725.00; found: 726.84 $[\text{M}+\text{Na}]^+$.

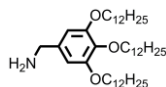


(3,4,5)12F8G1-2EO-Cl₄PBI (11). Into a stirred solution of carboxylic acid **14** (0.48 g, 0.30 mmol) in dry THF (12 mL) were added PPh_3 (0.16 g, 0.60 mmol), and dianhydride **10** (0.13 g, 0.18 mmol) under N_2 and stirred for 5 min. DIAD (0.12 g, 0.06 mmol) was added slowly and the reaction mixture was stirred for 16 h at 25 °C. The reaction mixture was concentrated and precipitated in MeOH. The crude product was purified by column chromatography (SiO_2 , 30% EtOAc in hexane) followed by precipitation from CH_2Cl_2 into MeOH to give the product as a red solid (0.35 g, 61%). Purity (HPLC): 99%+. ^1H NMR (500 MHz, CDCl_3), δ (ppm): 8.63 (s, 4H, Per-*H*), 7.29 (s, 4H, Ar*H*), 4.49 (t, $^3J = 5.6$ Hz, 4H, NCH_2), 4.47–4.38 (m, 4H, $\text{CH}_2\text{O}_2\text{C}$), 4.08 (t, $^3J = 5.7$ Hz, 8H, ArOCH_2), 4.02 (t, $^3J = 5.5$ Hz, 4H, ArOCH_2), 3.96–3.85 (m, 8H, OCH_2), 2.23–2.08 (m, 12H, OCH_2CH_2), 1.96–1.79 (m, 24H,

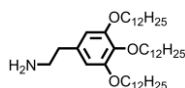
$\text{CH}_2\text{C}_8\text{F}_{17}$). ^{13}C NMR (126 MHz, CDCl_3), δ (ppm): 166.3, 162.4, 152.7, 142.1, 135.6, 133.2, 131.6, 128.8, 125.3, 123.5, 123.2, 108.4, 120.6–108.7 (several broad CF multiplets), 108.4, 72.8, 68.9, 68.6, 68.0, 64.4, 39.7, 31.0, 30.8, 30.6, 29.9, 28.9, 17.5, 17.3. MALDI-TOF (m/z): calc. for $[\text{C}_{118}\text{H}_{72}\text{Cl}_4\text{F}_{102}\text{N}_2\text{NaO}_{16}]^+$: 3873.19; found: 3874.97 $[\text{M}+\text{Na}]^+$.



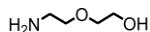
3,4,5-Tris(dodecyloxy)aniline (12a). This compound was synthesized according to a literature procedure.^{S8}



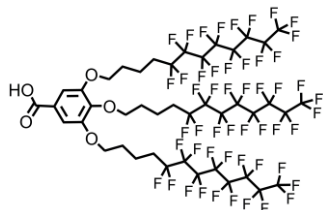
(3,4,5-Tris(dodecyloxy)phenyl)methanamine (12b). This compound was synthesized according to a literature procedure.^{S8}



2-(3,4,5-Tris(dodecyloxy)phenyl)ethan-1-amine (12c). This compound was synthesized according to a literature procedure.^{S8}



2-(2-Aminoethoxy)ethanol (13). This compound was purchased from Aldrich and used as received.



3,4,5-Tris((1H,1H,2H,2H,3H,3H,4H,4H-perfluorododecyl)oxy)benzoic acid (14). This compound was synthesized according to a literature procedure.^{S9}

4. Supporting XRD Analysis

Supporting Table ST1. XRD Analysis of Hydrogenated Dendronized Tetrachlorinated PBIs **8a–c** ($m = 0, 1, 2$) and Semifluorinated Dendronized Tetrachlorinated PBIs **9** ($m = 3$) and **11** ($m = 2\text{EO}$)

Compound	T (°C)	Phase ^a	a, b, c (Å) α, β, γ ^b	$d_{100}, d_{110}, d_{200}, d_{210}, d_{001}, d_{101}$ (Å) ^c $d_{100}, d_{110}, d_{200}, d_{220}, d_{201}, d_{211}$ (Å) ^d $d_{100}, d_{110}, d_{200}, d_{020}, d_{220}, d_{310}, d_{130}, d_{011}, d_{111}, d_{201}, d_{222}, d_{032}$ (Å) ^e $d_{210}, d_{400}, d_{420}, d_{101}, d_{211}, d_{132}$ (Å) ^f $d_{100}, d_{010}, d_{110}, d_{200}, d_{210}, d_{300}, d_{120}, d_{220}, d_{410}, d_{320}$ (Å) ^g $d_{121}, d_{221}, d_{002}, d_{012}, d_{122}, d_{402}$ (Å) ^h $d_{100}, d_{200}, d_{120}, d_{2-30}, d_{300}, d_{3-30}, d_{002}$ (Å) ⁱ $d_{110}, d_{200}, d_{020}, d_{320}, d_{400}, d_{240}, d_{530}, d_{700}, d_{640}, d_{810}, d_{001}, d_{111}, d_{121}$ (Å) ^j $d_{061}, d_{811}, d_{831}, d_{581}, d_{681}, d_{002}, d_{222}, d_{402}, d_{432}, d_{662}, d_{482}$ (Å) ^k $d_{100}, d_{1-10}, d_{010}, d_{200}, d_{110}, d_{1-20}, d_{2-20}, d_{3-10}, d_{210}, d_{4-20}, d_{2-30}$ (Å) ^l $d_{10}, d_{11}, d_{20}, d_{21}$ (Å) ^m
8a ($m = 0$)	190	$\Phi_{\text{h}}^{\text{k}}$	28.8, 28.8, 25.2 90°, 90°, 120°	25.2, 14.6, 12.6, 9.5, 19.1, 15.2 ^c
	125	$\Phi_{\text{tetra}}^{\text{k}}$	37.0, 37.0, 25.2 90°, 90°, 90°	37.2, 26.3, 18.6, 13.2, 15.1, 14.0 ^d
	40	$\Phi_{\text{c-o}}^{\text{k1}}$	37.3, 35.1, 25.1 90°, 90°, 90°	37.3, 25.6, 18.7, 17.6, 12.8, 11.7, 11.2, 20.4, 17.9, 15.0, 8.9, 8.5 ^e
	−10	$\Phi_{\text{c-o}}^{\text{k2}}$	38.2, 33.1, 25.1 90°, 90°, 90°	38.2, 25.0, 19.1, −, 12.5, 11.9, 10.6, −, 17.8, 15.2, −, 8.3 ^e 16.6, 9.6, 8.3, 21.0, 13.8, 8.1 ^f
8b ($m = 1$)	20	$\Phi_{\text{s-o}}^{\text{k}}$	47.3, 27.2, 17.3 90°, 90°, 90°	47.3, 27.2, 23.6, 23.7, 17.9, 15.8, 13.1, 11.8, 10.9, 10.3 ^g 10.4, 9.8, 8.7, 8.3, 7.2, 7.0 ^h
8c ($m = 2$)	70	$\Phi_{\text{m}}^{\text{k}}$	37.5, 39.0, 12.7 90°, 90°, 116°	33.7, 16.9, 13.3, 12.5, 11.2, 10.8, 6.4 ⁱ
	20	$\Phi_{\text{c-o}}^{\text{k}}$	53.1, 48.8, 12.9 90°, 90°, 90°	35.9, 26.6, 24.4, 14.3, 13.3, 11.1, 8.9, 7.6, 7.2, 6.6, 12.9, 12.1, 11.2 ^j 6.9, 5.9, 5.6, 4.9, 4.7, 6.5, 6.1, 5.8, 5.5, 4.4, 4.2 ^k
	20	$\Phi_{\text{m}}^{\text{k n}}$	42.5, 30.4, − 90°, 90°, 118°	37.5, 29.2, 26.8, 18.8, 18.2, 15.1, 14.6, 14.2, 12.8, 10.3, 10.1 ^l
9 ($m = 3$)	20	Φ_{h}	43.1, 43.1, − 90°, 90°, 120°	37.3, 21.6, 18.7, 14.1 ^m
	20	$\Phi_{\text{h}}^{\text{io(hc)}}$	49.5, 49.5, − 90°, 90°, 120°	42.9, 24.8, 21.4, 16.2 ^m
	120	$\Phi_{\text{h}}^{\text{io(hc)}}$	47.5, 47.5, − 90°, 90°, 120°	41.2, 23.8, 20.6, 15.6 ^m

^a Phase notation: $\Phi_{\text{h}}^{\text{k}}$ – columnar crystalline hexagonal phase; Φ_{h} – 2D columnar hexagonal phase with intracolumnar order; $\Phi_{\text{h}}^{\text{io(hc)}}$ – 2D tiled hexagonal phase with intracolumnar order; $\Phi_{\text{tetra}}^{\text{k}}$ – columnar crystalline tetragonal phase; $\Phi_{\text{c-o}}^{\text{k}}$ – columnar crystalline centered orthorhombic phase; $\Phi_{\text{s-o}}^{\text{k}}$ – columnar crystalline simple orthorhombic phase; $\Phi_{\text{m}}^{\text{k}}$ – columnar monoclinic crystalline phase; ^b Lattice parameters determined from fiber and powder X-ray diffractions. ^c experimental diffraction peaks d -spacing for the $\Phi_{\text{h}}^{\text{k}}$ phase. ^d experimental diffraction peaks d -spacing for the $\Phi_{\text{tetra}}^{\text{k}}$ phase. ^{e, f, j, k} experimental diffraction peaks d -spacing for the $\Phi_{\text{c-o}}^{\text{k}}$ phase. ^{g, h} experimental diffraction peaks d -spacing for the $\Phi_{\text{s-o}}^{\text{k}}$ phase. ^{i, l} experimental diffraction peaks d -spacing for the $\Phi_{\text{m}}^{\text{k}}$ phase. ^m experimental diffraction peaks d -spacing for the $\Phi_{\text{h}}^{\text{io}}$ and $\Phi_{\text{h}}^{\text{io(tile)}}$ phase. ⁿ Phase observed only in as prepared samples during first heating.

5. Reconstruction of Electron Density Maps and Selection of Phase Combinations

As originally published in ref. S10:

“Phase assignments were based on the physical merit of the reconstructed electron density maps; that is, showing a good separation of regions of different electron densities and being reconcilable to a physical model consistent with the dimensions and shape of the molecules.”

As originally published in the Supporting Information of ref. S10:

“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:

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

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:

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

When only a relative electron density fluctuation is of interest, 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 ϕ_{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 ϕ_{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).”

6. References for the Supporting Information

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