Supporting Information for

Board-like dibenzo[*fg,op*]naphthacenes: Synthesis, characterization, self-assembly, and liquid crystallinity

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Fig. S14 XRD of DBN(OC₁₀) in the SmA phase. The peaks correspond to ~29.2 and ~4.45 Å.





Experimental

Synthesis

General. Unless otherwise noted, all starting materials, reagents, and solvents were purchased from commercial sources and used without further purification. Anhydrous THF was obtained by distillation from sodium–benzophenone. Anhydrous CH_2Cl_2 was obtained by distillation from CaH_2 . NMR spectra were measured for $CDCl_3$, benzene- d_6 , or acetone- d_6 solutions using Bruker Avance 300 MHz or 500 MHz NMR. Chemical shifts are reported in δ (ppm) relative to TMS, with the residual solvent protons used as internal standards. Low resolution ESI and APCI mass spectra were recorded on Bruker Esquire ESI mass spectrometer. MALDI spectra were acquired on a Bruker Ultraflex MALDI spectrometer using dithranol or HABA as the matrix. Elemental Analysis results were obtained from Galbraith Laboratories, Inc.

Tetramer 1. A Schlenk vacuum tube was charged with 2,2'-dibromo-5,5'-dimethoxybiphenyl¹ (744 mg, 2.00 mmol), 2-chloro-4-methoxyphenylboronic acid (820 mg, 4.40 mmol), and Pd(PPh₃)₄ (92 mg, 0.08 mmol), then evacuated and backfilled with argon (3×). Degassed toluene (16.0 mL), ethanol (2.7 mL) and 2 M Na₂CO₃ (8.0 mL) were added under the positive pressure of argon. The Schlenk tube was sealed and heated at 90–100 °C for 2 days, then cooled, diluted with EtOAc (40 mL), and washed with water. The aqueous layer was acidified with 1 M HCl, then was extracted with EtOAc. The combined organic layers were washed with water and brine, dried over MgSO₄, filtered, and concentrated. Purification by flash chromatography (8:1 hexanes:EtOAc) gave 411 mg (83%) of 1 as an off-white foam: ¹H NMR (CDCl₃, 500 MHz) δ 3.77 (br s, 12H), 6.59-7.12 (br m, 12H), broadened because of slow conformational exchange, see Fig. S15; MS (ESI) calcd for C₂₈H₂₅Cl₂O₄ (M+H⁺) 495.1, found 495.2.

Tetramer 2. 1 M BBr₃ (in CH₂Cl₂, 8.00 mL) was added to a solution of 1 (495 mg, 1.00 mmol) in anhydrous CH₂Cl₂ (70 mL) at -78 °C; the mixture was allowed to warm to room temperature overnight. The reaction was quenched with slow addition of water, then the white precipitate was isolated by filtration. The organic layer from the filtrate was separated and the aqueous layer extracted with ethyl acetate (5×). The combined organic layers were washed with brine and concentrated. The crude product was purified by flash chromatography (1:1 hexanes:acetone) to afford 373 mg (85 %) of **2** as a white powder: ¹H NMR (acetone-d₆, 500 MHz) δ 6.55-6.98 (br m, 12H), 8.46 (br s, 4H), broadened because of slow conformational exchange, see Fig. S16; MS (ESI) calcd for C₂₄H₁₅Cl₂O₄ (M–H⁺) 437.0, found 437.1

General procedure for the synthesis of 3(OR). A Schlenk vacuum tube was charged with 2 (439 mg, 1.00 mmol), 1-bromoalkane (8.00 mmol), anhydrous K_2CO_3 (1.10 g, 8.00 mmol) and KI (33.2 mg, 0.20 mmol), then evacuated and backfilled with argon (3×). Anhydrous DMF (10 mL) was added and the Schlenk tube was sealed and heated at 90 °C for 2 days. The mixture was allowed to cool to r.t., diluted with ethyl ether (20 mL), and poured into water (30 mL). The organic layer was separated and the aqueous layer was extracted with ethyl ether (3×). The organic layers were combined, washed with brine, dried over MgSO₄, filtered, and concentrated.

Tetramer 3(OC₆). Using 1-bromohexane as the starting material, purification by flash chromatography (8:1 hexanes:EtOAc) gave 357 mg (46%) 3(OC₆) as an off-white foam: ¹H NMR (CDCl₃, 500 MHz) δ 0.92 (m, 12H), 1.26-1.59 (m, 24H), 1.75 (m, 8H), 3.89 (br s, 8H), 6.57-7.11 (br m, 12H), broadened because of slow conformational exchange, see Fig. S17; MS (APCI) calcd for C₄₈H₆₅Cl₂O₄ (M+H⁺) 775.4, found 775.5.

Tetramer 3(OC₈). Using 1-bromooctane as the starting material, purification by flash

chromatography (10:1 hexanes:EtOAc) gave 586 mg (66%) $3(OC_8)$ as an off-white foam: ¹H NMR (CDCl₃, 500 MHz) δ 0.90(m, 12H), 1.30-1.43 (m, 40H), 1.75 (m, 8H), 3.89 (br s, 8H), 6.57-7.11 (br m, 12H), broadened because of slow conformational exchange, see Fig. S18; MS (APCI) calcd for $C_{56}H_{81}Cl_2O_4$ (M+H⁺) 887.6, found 887.8.

Tetramer 3(OC₁₀). Using 1-bromodecane as the starting material, purification by flash chromatography (12:1 hexanes:EtOAc) gave 704 mg (70%) 3(OC₁₀) as an off-white foam: ¹H NMR (CDCl₃, 500 MHz) δ 0.90 (m, 12H), 1.29-1.44 (m, 56H), 1.76 (m, 8H), 3.90 (br s, 8H), 6.57-7.11 (br m, 12H), broadened because of slow conformational exchange, see Fig. S15; MS (APCI) calcd for C₆₄H₉₇Cl₂O₄ (M+H⁺) 999.7, found 999.7.

Tetramer 3(OC₁₂). Using 1-bromododecane as the starting material, purification by flash chromatography (20:1 hexanes:EtOAc) gave 690 mg (62%) 3(OC₁₂) as an off-white foam: ¹H NMR (CDCl₃, 500 MHz) δ 0.89(m, 12H), 1.27-1.43 (m, 72H), 1.75 (m, 8H), 3.89 (br s, 8H), 6.57-7.12 (br m, 12H), broadened because of slow conformational exchange, see Fig. S20; MS (APCI) calcd for C₇₂H₁₁₃Cl₂O₄ (M+H⁺) 1111.8, found 1111.8.

Tetramer 3(OC_{br}). Using 1-bromo-3,7-dimethyloctane as the starting material, purification by flash chromatography (12:1 hexanes:EtOAc) gave 500 mg (50 %) $3(OC_{br})$ as an off-white foam: ¹H NMR (CDCl₃, 500 MHz) δ 0.86-0.94(m, 12H), 1.16-1.79 (m, 64H), 3.92 (br s, 8H), 6.58-7.12 (br m, 12H), broadened because of slow conformational exchange, see Fig. S21; MS (APCI) calcd for C₆₄H₉₇Cl₂O₄ (M+H⁺) 999.7, found 999.7.

General procedure for the synthesis of DBN(OR). A photochemical reaction vessel was charged with 3(OR) (0.1 mmol) and 10 mL anhydrous benzene. The solution was degassed by bubbling with argon for 30 min and then irradiated under UV (medium-pressure mercury lamps) for 2 days. The mixture was then concentrated.

Dibenzo[*fg,op*]**naphthacene DBN(OC**₆). Recrystallization from toluene/ethanol then from toluene gave 32 mg (45%) of **DBN(OC**₆) as yellow fibers: see text and Fig. S6 for phase behavior; ¹H NMR (C₆D₆, 500 MHz) δ 0.93 (t, 12H, *J* = 6.6 Hz), 1.34 (m, 18H), 1.45 (m, 4H), 1.55 (m, 4H), 1.85 (m, 4H), 1.90 (m, 4H), 3.92 (t, 4H, *J* = 6.6 Hz), 4.17 (t, 4H, *J* = 6.6 Hz), 7.37 (d, 2H, *J* = 8.9 Hz), 7.48 (dd, 2H, *J* = 8.9 Hz), 8.60 (t, 4H, *J* = 8.6 Hz), 9.67 (s, 2H), see Fig. S22; MS (MALDI) calcd for C₄₈H₆₂O₄ 702.46, found 702.55; anal. calcd for C₄₈H₆₂O₄ C 82.01, H 8.89, found C 81.74, H 8.89.

Dibenzo[*fg*,*op*]**naphthacene DBN(OC**₈). Recrystallization from toluene/ethanol then from toluene gave 48 mg (59%) of **DBN(OC**₈) as yellow fibers: see text and Fig. S6 for phase behavior; ¹H NMR (C₆D₆,

500 MHz) δ 0.93 (m, 12H), 1.32 (m, 34H), 1.49 (m, 4H), 1.58 (m, 4H), 1.91 (m, 8H), 3.99 (t, 4H, *J* = 6.4 Hz), 4.21 (t, 4H, *J* = 6.4 Hz), 7.41 (d, 2H, *J* = 8.9Hz), 7.47 (dd, 2H, *J* = 8.5 Hz, 2.1 Hz), 8.59 (t, 4H, *J* = 8.7 Hz), 9.67 (s, 2H), see Fig. S23; MS (MALDI) calcd for C₅₆H₇₈O₄ 814.59, found 814.52; anal. calcd for C₅₆H₇₈O₄ C 82.51, H 9.64, found C 82.09, H 9.58.

Dibenzo[*fg,op*]**naphthacene DBN(OC**₁₀). Recrystallization from toluene/ethanol then from toluene gave 57 mg (62%) of **DBN(OC**₁₀) as yellow fibers: see text and Fig. S6 for phase behavior; ¹H NMR (C₆D₆, 500 MHz, 50 °C) δ 0.93 (m, 12H), 1.33 (m, 50H), 1.52 (m, 4H), 1.61 (m, 4H), 1.93 (m, 8H), 4.00 (t, 4H, *J* = 6.8 Hz), 4.22 (t, 4H, *J* = 6.2 Hz), 7.41 (d, 2H, *J* = 8.7Hz), 7.46 (d, 2H, *J* = 9.2Hz), 8.59 (t, 4H, *J* = 9.1Hz), 9.67 (s, 2H), see Fig. S24; MS (MALDI) calcd for C₆₄H₉₄O₄ 926.72, found 926.70; anal. calcd for C₆₄H₉₄O₄ C 82.88, H 10.22, found C 82.75, H 10.15.

Dibenzo[*fg,op*]**naphthacene DBN(OC**₁₂). Recrystallization from toluene/ethanol then from toluene gave 70 mg (67%) of **DBN(OC**₁₂) as yellow fibers: see text and Fig. S6 for phase behavior; ¹H NMR (C₆D₆, 500 MHz, 50 °C) only trace peaks detected because of poor solubility, see Fig. S25; MS (MALDI) calcd for C₇₂H₁₁₀O₄ 1038.84, found 1038.76; anal. calcd for C₇₂H₁₁₀O₄ C 83.18, H 10.66, found C 82.81, H 10.47.

Dibenzo[*fg,op*]**naphthacene DBN**(**OC**_{br}). Recrystallization from toluene/ethanol gave 37 mg (40%) yellow crystals: mp 104.0 °C; ¹H NMR (C₆D₆, 500 MHz) δ 0.93 (m, 24H), 1.06 (d, 4H *J* = 6.7 Hz), 1.24–1.87 (m, 44H), 2.06 (m, 4H), 4.05 (m, 4H), 4.29 (m, 4H), 7.40 (d, 2H, *J* = 8.9 Hz), 7.48 (dd, 2H, *J* = 8.9 Hz, 2.5 Hz), 8.59 (dd, 4H, *J* = 8.9 Hz, 2.5 Hz), 9.68 (d, 2H, *J* = 2.5 Hz), see Fig. S26; ¹³C NMR (C₆D₆, 125 MHz) δ 19.9, 20.0 (×2), 22.9, 23.0, 25.2, 25.3, 28.4 (×2), 30.5 (×2), 37.2, 37.3, 37.8, 38.0, 39.7 (×2), 113.1, 113.3, 116.8, 119.6, 121.8, 124.7, 124.8 (×2), 125.4, 130.9, 156.2, 158.1, see Fig. S27; MS (MALDI) calcd for C₆₄H₉₄O₄ 926.72, found 926.83.

Characterization

UV/vis spectra were recorded using a Perkin Elmer Lambda 35 spectrophotometer. Fluorescence spectra were recorded using a Perkin Elmer LS 55 fluorescence spectrophotometer, and are corrected for emission. The quantum yield of **DBN(OC**_{br}) was determined in nitrogen-sparged cyclohexane according to the standard procedure. 9,10-Diphenylanthracene in cyclohexane ($\Phi_f = 0.92$) was used as the standard, which was cross-checked against quinine bisulfate in 0.1 N H₂SO₄ ($\Phi_f = 0.54$). Absorbances of the sample solutions were kept below 0.50 (10 mm cuvettes) to avoid the inner filter effect. Measurements were performed at room temperature, with both sample and reference solutions excited at the same wavelength (366 nm). Cyclic voltammetry was carried out using a CH Instruments CHI600D Electrochemical Analyzer in conjunction with a three electrode cell, using a Pt disc working electrode, a Pt wire as counter electrode, and another Pt wire as pseudo-reference electrode. The experiment was

calibrated against ferrocene as an internal standard. SEM measurements (Fig. S3) were performed in an Zeiss Supra 35 VP FEG SEM, operated at 2.0 kV at different magnitudes. DSC was performed using a TA Instruments Q20 Differential Scanning Calorimeter fitted with an RCS20 cooling unit; samples were scanned at a heating rate of 10 °C/min (for mp) or 5 °C/min (for liquid crystals). Polarized microscopy was performed using an Olympus BX51 polarizing optical microscope.

Nanobelt Self-Assembly and Testing of **DBN(OC**₁₂)

The nanobelts of $DBN(OC_{12})$ were prepared though a gelation process in chloroform. In a typical process, 5.0 mg $DBN(OC_{12})$ was added to 2 mL chloroform. Then the mixture was heated to boiling, at which point the system turned into a light yellow transparent solution. With cooling in air (room temperature), the solution became opaque. After 10 min, the gel process was complete.

SEM Sample Preparation. The gel was dispersed in 10 mL THF, and the mixture dropcast onto a silicon wafer and dried in ambient air. A FEI NanoNova Scanning Electron Microscope was used to characterize the morphology of nanobelts.

AFM Sample Preparation. The gel was dispersed in 10 mL THF, and the mixture dropcast onto a silicon wafer and dried in ambient air. A Veeco DiMultiMode V AFM was used to characterize the morphology of nanobelts. The scan area is 50×50 µm.

Optical Microscopy. The gel was dispersed in 10 mL THF, and the mixture dropcast onto a clean glass slide and dried in ambient air. We used Leica DMI4000B microscope to characterize the morphology of nanobelts.

Photocurrent Measurement. We dropcast the dispersed **DBN**(**OC**₁₂) fibers onto the electrode to test the dark- and photo-current by using Agilent 4156C Precision Semiconductor Parameter Analyzer. The electrode gap was 5 μ m and length was 20 μ m. All the tests were done under ambient conditions. When testing the photocurrent, the light intensity is 65.9 mW·cm⁻². We used 100 μ L of a 0.15 × 10⁻³ mol·L⁻¹ dichloromethane PDI solution to drop cast onto the as-prepared **DBN**(**OC**₁₂) electrodes to dope with the PDI molecule. The device was dried in air at room temperature.

X-Ray Diffraction

The samples **DBN(OR)** were contained in quartz capillaries of 1.5 mm diameter for XRD measurements. The capillaries were sealed with epoxy. X-ray scattering measurements were performed using the Rigaku Screen Machine with microfocus sealed X-ray tube with copper anode ($\lambda = 1.542$ Å) (**DBN(OC**₁₀)) and at the synchrotron source at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL) (**DBN(OC**₆), **DBN(OC**₈), **DBN(OC**₁₂)). The former is equipped

with a Mercury 3 CCD detector and the sample was placed at 65.36 mm from it. The measurements at BNL were carried out at Sector X6B using 12 KeV X-rays ($\lambda = 1.03297$ Å). The 2D diffraction patterns were taken using high resolution image plate detector PI-SCX4300 positioned 255.2 mm away from the sample.

The capillaries containing the compounds were placed between a pair of rare earth permanent magnets inside a hot stage (INSTEC HS402) and sample temperature controlled with a precision of \pm 0.1 °C. The 2D X-ray patterns were analyzed using the software FIT2D² after subtracting the background measured with an empty capillary in the sample position. The data was calibrated against silver behenate or silicon standards traceable to the National Institute of Standards and Technology.

DFT Geometry Optimization of the Methoxy-Substituted DBN Core

DFT calculations were carried out using Gaussian 09 (Rev. B.01) on Miami University's Redhawk computer cluster. Calculated geometries were visualized using VMD.³ The geometry of **DBN(OMe)** (i.e., Fig. 4) was optimized at the B3LYP/6-31G(d) level yielding a C_2 -symmetric structure with a total energy of $-1381.135447 E_h$. Cartesian atomic coordinates are given in Table S1. Vibrational frequency analysis confirms that this geometry has no imaginary frequencies, and gives a zero-point correction of 0.432722 E_h (unscaled).

NMR Spectra of Synthesized Compounds



Fig. S16 ¹H NMR spectrum (500 MHz, CDCl₃) of compound 1.











Fig. S22 ¹H NMR spectrum (500 MHz, CDCl₃) of compound 3(OC_{br}).



Fig. S23 ¹H NMR spectrum (500 MHz, benzene-*d*₆) of compound **DBN(OC**₆).



Fig. S24 ¹H NMR spectrum (500 MHz, benzene-*d*₆) of compound **DBN(OC**₈).







Fig. S29 gCOSY NMR spectrum (500 MHz, benzene- d_6) of compound DBN(OC_{br}).









NMR Analysis of DBN(OC_{br})

The aromatic ¹³C NMR signals of **DBN(OC**_{br}) were unambiguously assigned using the HSQC and HMBC (and COSY) spectra, then compared with isotropic shieldings calculated for the optimized geometry of the methoxy-substituted derivative (Fig. 4) using the GIAO method⁴ at the PCM(benzene)/B3LYP/6-31G(d,p) level. The isotropic shieldings were converted to chemical shifts using the (commonly used) scaling method.⁵ The agreement between the DFT and experimental data is excellent, with and R^2 of 0.99 and a RMS error of 1.6 ppm. Much of the discrepancy is associated with

the positions *ortho* to the alkoxy groups (6 and 9), and presumably reflects the simplification of the alkoxy side-chains to methoxy groups in the computational geometry.

Table S1 Experimental (DBN(OC_{br})) and calculated (methoxy-substituted core) ¹³C NMR chemical shifts.





Fig. S32 Plot of calculated aromatic chemical shifts for the methoxy-substituted DBN core vs the experimental shifts for DBN(OC_{br}).

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