Supporting Information
Facile synthesis and X-ray structure of alkoxy-functionalized
dibenzo[*fg,op*]naphthacenes

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General. ¹H-NMR and ¹³C-NMR spectra: Bruker-WH-250, –AM-400 or –DRX-500 spectrometer. High resolution MS (HRMS): Finnigan MAT 90 spectrometer, ionization potential 70 eV. Field-desorption (FD) mass spectra: VG ZAB 2-SE-FPD. UV spectra: Perkin Elmer Lambda 19. Thin-layer chromatography: aluminum plates precoated with 5735 silica gel 60 PF₂₅₄ (Merck). Column chromatography: merck silica gel 60 (230-400 mesh). Radial chromatography: Chromatotron (Harrison Research Europe, Muttentz) using glass plates coated with 4 mm silica gel 60 PF₂₅₄ containing gypsum (Merck).

1a: Powdered NaOH (0.5 g 12.5 mmol), 2-bromoacetophenone (2.49 g, 12.5 mmol) and p-tolylaldehyde (0.75 g, 6.3 mmol) were mixed together with a pestle and mortar for 25 min. The highly viscous yellow mixture was dissolved in Et₂O (100 mL) and water, the organic phase was separated and washed with H₂O (3 × 50 mL), brine (3 × 50 mL) and dried over MgSO₄, and the solvent was removed in *vacuo*. The residue was purified by radial chromatography (*R*_f = 0.23; petroleum ether/CH₂Cl₂ 1:1) to yield **1a** (1.03 g, 33 %) as a highly viscous yellow oil. C₂₄H₂₀O₂Br₂ (500.22); Anal. calcd: C 57.63, H 4.03; found: C 57.56, H 4.08; EI-MS: *m/z* = 500 (*M*⁺+2; 100 %); HRMS (FAB): calcd for C₂₄H₂₀O₂Br₂ (*M*+1): 498.9909, found: 498.9916; ¹H-NMR (250 MHz; CD₂Cl₂): δ = 7.55 (m, 2 H, Ar-H), 7.25-6.91 (m, 10 H, Ar-H), 3.85 (m, 1 H, CH), 3.42-3.12 (m, 4 H, 2 CH₂CO), 2.19 (s, 3 H, CH₃); ¹³C-NMR (62.9 MHz; CDCl₃): δ = 202.36, 141.44, 139.61, 136.27, 133.49, 131.43, 129.18, 128.68, 128.43, 127.44, 127.28, 118.52, 48.62, 36.68, 20.96.

2a: Under an argon atmosphere, a mixture of **1a** (950 mg, 1.9 mmol), chalcone (395 mg, 1.9 mmol) and BF₃·OEt₂ (7 mL) was stirred at 100 °C for 2 h, then cooled to RT, and diluted with Et₂O (10 mL). After 12 h, the yellow precipitate was filtered off and washed thoroughly with Et₂O to yield **2a** (960 mg, 89 %) as a yellow solid. mp: 245 °C (dec.); C₂₄H₁₇BBBr₂F₄O (568.00); Anal. calcd: C 50.75, H 3.02; found: C 50.44, H 2.96; ¹H-NMR (250 MHz; CD₂Cl₂): δ = 8.69 (s, 2 H, Ar-H), 8.12-7.91 (m, 4 H, Ar-H), 7.89- 7.88 (m, 2 H, Ar-H), 7.69-7.56 (m, 6 H, Ar-H), 2.55 (s, 3 H, CH₃); ¹³C-NMR (100.6 MHz; CD₂Cl₂): δ = 171.97, 166.35, 149.97, 135.42, 135.21, 133.24, 131.88, 130.48, 130.39, 129.53, 129.27, 122.32, 120.12, 22.27.

3a: A mixture of **2a** (950 mg, 1.67 mmol), sodium 4-methoxyphenylacetate (1.57 g, 8.36 mmol) [prepared from 4-methoxyphenylacetic acid and sodium methylate (0.5 M) in methanol and subsequent evaporation of the solvent] in acetic anhydride (9 mL) was stirred at 150 °C for 2 h and then the acetic anhydride removed under *vacuo*. The residue was dissolved in Et₂O (100 mL), washed with 10 % aqueous NaOH (3 × 20 mL), H₂O (3 × 20 mL) and brine (3 × 20 mL), dried over MgSO₄ and then the solvent was removed in *vacuo*. The residue was purified by radial chromatography (*R_f* = 0.3; petroleum ether/CH₂Cl₂ 4:1) to yield **3a** (360 mg, 37 %) as colourless crystals. mp: 98 °C; C₃₂H₂₄OBr₂ (cal. 584.34); EI-MS: *m/z* = 584 (M⁺+2, 100 %); HRMS (EI): calcd for C₃₂H₂₄OBr₂: 582.0194, found: 582.0206; ¹H-NMR (250 MHz; CD₂Cl₂): δ = 7.49 (m, 6 H, Ar-H), 7.12 (m, 8 H, Ar-H), 6.82 (m, 2 H, Ar-H), 6.35 (m, 2 H, Ar-H), 3.60 (s, 3 H, OCH₃), 2.31 (s, 3 H, CH₃); ¹³C-NMR (100.6 MHz; CD₂Cl₂): δ = 158.13, 142.97, 142.80, 142.00, 141.91, 138.87, 137.86, 132.63, 132.54, 132.49, 132.27, 132.16, 131.76, 131.16, 129.87, 128.68, 128.62, 128.32, 127.05, 126.85, 124.13, 124.00, 112.53, 112.24, 29.97, 21.11.

4a: Under an argon atmosphere, PdCl₂(PPh₃)₂ (53 mg) was added to a solution of 1,8-diazabicyclo[5.4.0]undec-7-ene (208 mg) and **3a** (200 mg, 0.34 mmol) in dry N,N-dimethylacetamide (5 mL, Acros Organics, extra dry solvents, used as received), and the mixture was stirred at 160 °C for 12 h. The slightly tan solution (containing precipitated palladium black) was cooled to RT, poured into CH₂Cl₂ (200 mL), washed with H₂O (3 × 40 mL), and brine (3 × 20 mL), and dried over MgSO₄. After removing of the solvent in *vacuo* the residue was purified by recrystallization (two times) from CHCl₃ to yield **5a** (60 mg, 41.8 %) as slightly yellow crystals (*R_f* = 0.45; petroleum ether/CH₂Cl₂ 2:1). mp: 264 °C; C₃₂H₂₂O (422.167); EI-MS: *m/z* = 422.1 (M⁺, 100 %); HRMS (EI): calcd for C₃₂H₂₂O: 422.1670, found: 422.1662; ¹H-NMR (250 MHz; C₂D₂Cl₄): δ = 9.07 (s, 2 H, Ar-H), 8.91 (m, 2 H, Ar-H), 8.77 (m, 2 H, Ar-H), 8.42 (s, 2 H, Ar-H), 7.90 (d, ³*J*(H, H) = 7.6 Hz, 2 H, Ar-H), 7.82 (m, 4 H, Ar-H), 7.46 (d, ³*J*(H, H) = 7.9 Hz, 2 H, Ar-H), 4.21 (s, 3 H, OCH₃), 2.51 (s, 3 H, CH₃); ¹³C-NMR (100.6 MHz; C₂D₂Cl₄): δ = 157.99, 138.58, 137.92, 137.38, 130.99, 130.12, 129.76, 129.53, 128.67, 127.78, 127.60, 127.54, 123.67, 123.64, 122.67, 120.14, 118.37, 107.12, 55.68, 21.16; UV: λ_{max} (THF): 294 nm.

^1H NMR and ^{13}C NMR spectra of **4a**:

Figure 1a. Top view onto the stacks of **4a**. The columns of **4a** form double layers of the condensed aromatic parts of the molecules separated by layers of the attached disordered phenyl rings.

Figure 1b: Side view onto the stacks of **4a** displaying the herringbone packing motif of the infinite stacks.