Supplementary Information

Conformational Polymorphism of 1,8-Dipyridynaphthalene and Encapsulation of Chains of Fused Cyclic Water Pentamers in a Hydrophobic Crystal Environment

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CCDC 268403 (1-(H2O)3), 268402 (form II) and 268401 (form I) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.uk/conts/retrieving.htm or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk).

All chemicals were of reagent grade and were purchased from Aldrich. All reactions were carried out under nitrogen atmosphere under anhydrous conditions. Flash chromatography was carried out on SiO2 (Merck Kieselgel 60, particle size 0.032-0.063 mm). GC-MS was performed using a Fison Instruments MD800 capillary GC-Mass spectrometer. NMR spectra were obtained at 300 MHz (1H NMR) and 75 MHz (13C NMR) on a Varian FT-NMR spectrometer using CDCl3 as the solvent. Chemical shifts are reported in ppm relative to TMS.

Preparation of 1,8-Dipyridynaphthalene 1

A solution of 1,8-diiodonaphthalene (0.6 g, 1.58 mmol), 4-trimethylstannylpyridine (1.0 g, 4.14 mmol), and tetrakis(triphenylphosphane)palladium(0) (100 mg, 5.5 mol%) in 3 mL anhydrous DMF was refluxed for 5 h. The reaction mixture was allowed to cool to room temperature, poured into 10% NH4OH, and extracted with CH2Cl2. The combined organic layers were washed...
with water, dried over MgSO₄, and the filtrate was concentrated under reduced pressure. Recrystallization from EtOAc afforded 1 (300 mg, 1.06 mmol, 67%) as light yellow crystals (mp 279-280 °C). ¹H NMR: δ 6.93 (dd, J = 1.7 Hz, J = 4.4 Hz, 4H), 7.43 (dd, J = 1.1 Hz, J = 7.2 Hz, 2H), 7.62 (dd, J = 1.1 Hz, J = 8.2 Hz, 2H), 8.04 (dd, J = 7.2 Hz, J = 8.2 Hz, 2H), 8.23 (dd, J = 1.7 Hz, J = 4.4 Hz, 4H). ¹³C NMR: δ 14.4, 125.5, 128.0, 129.7, 131.1, 135.2, 137.0, 148.8, 150.3. EI-MS (70 eV): m/z (%) = 282 (100) [M⁺], 254 (25) [M⁺-CH₂N], 226 (19) [M⁺-2 CH₂N], 202 (26) [M⁺-H, -Py], 127 (25) [M⁺-H, -2Py]. Anal. Calc. for C₂₀H₁₄N₂: C, 85.00; H, 5.00; N, 9.92. Found: C, 84.66; H, 5.08; N, 9.91.

Preparation of 4-Trimethylstannylpyridine.

Commercially available 4-bromopyridine hydrochloride (3.1 g, 15.4 mmol) was partitioned between 2N NaOH and CH₂Cl₂. The organic layers were dried over anhydrous MgSO₄ and CH₂Cl₂ was removed under reduced pressure. A yellow oil of 4-bromopyridine (2.4 g, 15.2 mmol, 99 %) was obtained and used without further purification. The crude material was dissolved in 20 mL anhydrous Et₂O and cooled to –78°C. n-Butyllithium in hexanes (10.4 mL, 1.6M) was added and the reaction mixture was stirred for one hour. A solution of trimethylstannyl chloride (3.8 g, 19 mmol) in 10 mL anhydrous Et₂O was added dropwise. The mixture was allowed to stir at room temperature for 5 hours. Following the work-up procedure described above gave a brown residue. Purification by flash chromatography (EtOAc/hexanes/Et₃N 250:250:1) afforded 4-trimethylstannylpyridine (2.41g, 10.0 mmol, 66%) as a light orange oil. ¹H NMR: δ 0.33 (s, 9H), 7.39 (dd, J = 1.5 Hz, J = 4.2 Hz, 2H), 8.51 (dd, J = 1.5 Hz, J = 4.2 Hz, 2H). ¹³C NMR: δ -9.6, 131.0, 148.3, 152.8. EI-MS (70 eV): m/z (%) = 239
(29) [M^+], 224 (100) [M^+-Me], 209 (34) [M^+-2Me], 194 (68) [M^+-3Me], 161 (18) [Me_3Sn], 131 (50) [MeSn], 116 (30) [Sn], 78 (17) [C_5H_4N].

TGA of 1-(H_2O)_3

Thermogravimetric analysis was performed under nitrogen with a heating rate of 5°C/min using a TA Instruments TGA 2050 Analyzer.