Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

The Ouroborand: A Cavitand with a Coordination-Driven Switching Device**

*Fabien Durola and Julius Rebek, Jr.**

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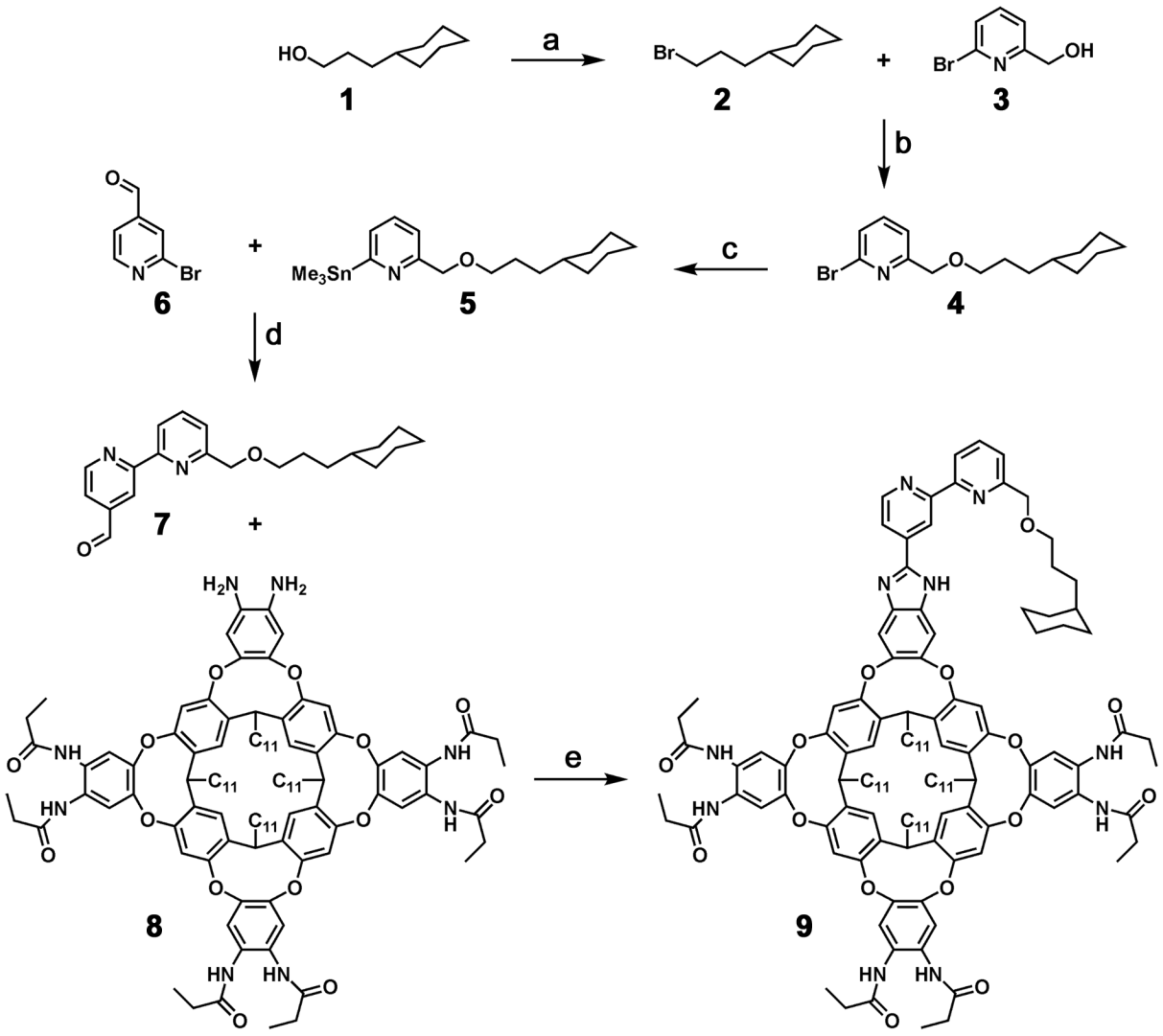
Synthesis scheme



global strategy for the synthesis of the ouroborand **9**

a : PBr_3, 0°C 15 min, rt 2 h, 100°C 1.5 h, 100%
b : NaH, THF, rt 2 h, 75°C 16 h, 26%
c : BuLi, toluene, -20°C, -78°C 2 h, Me_3SnCl, -78°C 1 h, rt, 55%
d : $Pd(PPh_3)_4$, toluene, 110°C 48 h, 75%
e : dioxane, rt 30 min, 100°C 16 h, 67%

Instrumentation

Proton Nuclear Magnetic Resonance (^{1}H NMR) spectra were acquired on a Bruker DRX-600 (600 MHz) spectrometer. The spectra were referenced to residual proton-solvent references (^{1}H : CD_3CN : 1.94 ppm, CD_2Cl_2 : 5.32 ppm, $CDCl_3$: 7.26 ppm, mesitylene d^{12} : 6.64 ppm).

Mass spectra were obtained by using a Agilent ESI-QQQ spectrometer (ES-MS) or a Bruker Daltonics High Resolution Q-FTMS spectrometer (High Resolution ES-MS).

Synthesis

Diamino cavitand **8** is synthesized following a previously described 5 step procedure.
reference : A. R. Renslo, J. Rebek, Jr. *Angew. Chem. Int. Ed. Engl.* **2000**, *39*, 3281-3283.

(3-bromopropyl)cyclohexane (**2**) :
To 1.87 g (13 mmol) of 3-cyclohexyl-1-propanol **1** was added dropwise 0.67 mL (7 mmol) of phosphorus tribromide. The mixture was stirred at 0°C for 15 min, at room temperature for 2 h, and then at 100°C for 1.5 h. The reaction was then quenched with 20 mL of ice, diluted with 20 mL of brine, and extracted with ether. The organic layer was washed with brine, dried over Na_2SO_4, filtered, and the solvent was evaporated to give 2.71 g (100%) of the brominated compound **2** as a colorless oil.
^{1}H NMR (600 MHz, $CDCl_3$) : δ (ppm) = 3.42 (t, 2H, J = 6.9 Hz), 1.92-1.87 (m, 2H), 1.73-1.66 (m, 5H), 1.35-1.22 (m, 6H), 1.95-1.89 (m, 2H).
ESI-MS m/z = 204.02 (calculated 204.05 for $C_9H_{17}Br$).

2-bromo-6-((3-cyclohexylpropoxy)methyl)pyridine (**4**) :
To a stirred solution of (6-bromopyridin-2-yl)methanol **3** (960 mg, 5.12 mmol) in dry THF under nitrogen was added a suspension of NaH (60% dispersion in mineral oil, 245 mg, 6.1 mmol) in dry THF. The reaction mixture was stirred at room temperature for 1.5 h. Brominated compound **2** (1050 mg, 5.1 mmol) was then added and the reaction mixture was refluxed overnight. The reaction mixture was then cooled, and residual sodium hydride quenched by addition of a small amount of methanol. The solvent was removed under vacuum. The crude product was purified by chromatography, on silica gel with dichloromethane as eluent, to give the title product **4** (411 mg, 26% yield) as a yellowish viscous oil.
^{1}H NMR (600 MHz, $CDCl_3$) : δ (ppm) = 7.58 (t, 1H, J = 7.6 Hz), 7.46 (d, 1H, J = 7.6 Hz), 7.39 (d, 1H, J = 7.8 Hz), 4.62 (s, 2H), 3.56 (t, 2H, J = 6.7 Hz), 1.75-1.65 (m, 7H), 1.30-1.15 (m, 6H), 0.94-0.88 (m, 2H).
HR ESI-MS m/z = 312.0957 (calculated 312.0957 for $C_{15}H_{22}BrNO+H^+$).

2-((3-cyclohexylpropoxy)methyl)-6-(trimethylstannyl)pyridine (**5**) :
Brominated pyridine **4** (410 mg, 1.3 mmol) was dissolved in 20 mL of toluene. n-BuLi (0.6 mL, 2.5 M in hexane, 1.5 mmol) was added dropwise onto the solution maintained at -20°C during the beginning of the addition. The mixture turned red and the temperature was lowered to -78°C. The mixture was stirred at -78°C for 2 h and then a solution of $ClSnMe_3$ (315 mg,

1.6 mmol) in toluene (4 mL) was carefully added. At the end of the addition, the yellow solution was stirred for one additional hour at -78°C and then allowed to warm up to room temperature and was stirred two more hours. Toluene was evaporated and the crude product taken up in CH_2Cl_2. Insoluble salts were filtered off on a sintered glass. The filtrate was evaporated to dryness and the resulting yellow oil was submitted to a very fast chromatography on alumina with Et_2O/hexanes (2:3) as the eluent to afford the title tin compound (yellow oil, 287 mg, 55%).
^{1}H NMR (600 MHz, $CDCl_3$) : δ (ppm) = 7.54 (t, 1H, J = 7.6 Hz), 7.34 (d, 1H, J = 7.8 Hz), 7.32 (d, 1H, J = 7.8 Hz), 4.67 (s, 2H), 3.57 (t, 2H, J = 6.7 Hz), 1.75-1.65 (m, 7H), 1.31-1.18 (m, 6H), 0.94-0.89 (m, 2H), 0.35 (s, 9H).
HR ESI-MS m/z = 398.1505 (calculated 398.1506 for $C_{18}H_{31}NOSn+H^+$).

6'-((3-cyclohexylpropoxy)methyl)-2,2'-bipyridine-4-carboxaldehyde (**7**) :
Stannylpyridine **5** (287 mg, 0.72 mmol) and 2-bromopyridine-4-carboxaldehyde **6** (161 mg, 0.87 mmol) were dissolved in dry toluene (15 mL). The solution was degassed three times, $Pd(PPh_3)_4$ (83 mg, 0.07 mmol) was added under a N_2 stream and the mixture was degassed three times again. The solution was heated at reflux for 48 h. Pd black was filtered off and the solvent was evaporated. The crude product was submitted to a chromatography on silica gel with dichloromethane/methanol (99:1) as the eluent to afford the title bipyridine compound (yellow viscous oil, 183 mg, 75%). This compound is luminescent.
^{1}H NMR (600 MHz, $CDCl_3$) : δ (ppm) = 10.22 (s, 1H), 8.92 (d, 1H, J = 4.8 Hz), 8.87 (d, 1H, J = 1.5 Hz), 8.35 (d, 1H, J = 7.8 Hz), 7.89 (t, 1H, J = 7.8 Hz), 7.74 (dd, 1H, J = 4.8, 1.5 Hz), 7.57 (d, 1H, J = 7.7 Hz), 4.76 (s, 2H), 3.62 (t, 2H, J = 6.7 Hz), 1.77-1.66 (m, 7H), 1.34-1.16 (m, 6H), 0.96-0.90 (m, 2H).
HR ESI-MS m/z = 339.2066 (calculated 339.2067 for $C_{21}H_{26}N_2O_2+H^+$).

Ouroborand (**9**) :
To the hexa-amide diamino cavitand **8** (165 mg, 0.0894 mmol) and bipyridine **7** (30 mg, 0.089 mmol) in a 50 mL sealed tube was added freshly distilled dioxane (1 mL). The mixture was stirred at room temperature for 30 min, and then at 100 ºC for 16 h. It was allowed to cool to room temperature, and all the volatiles were evaporated and concentrated *in vacuo*. Purification was made by column chromatography on silica gel with dichloromethane/methanol (99:1) as the eluent to afford the desired compound **9** as a white solid (130 mg, 67%).
^{1}H NMR (600 MHz, mesitylene d^{12}) : δ (ppm) = 12.36 (s, 1H), 9.87 (s, 1H), 9.85 (s, 1H), 9.78 (s, 1H), 9.75 (s, 1H), 8.87 (s, 1H), 8.61 (s, 1H), 8.58 (d, 1H, J = 4.7 Hz), 8.42 (d, 1H, J = 7.8 Hz), 8.15 (s, 1H), 7.84 (s, 1H), 7.79 (s, 1H), 7.71 (s, 1H), 7.65 (dd, 1H, J = 4.8, 1.6 Hz), 7.59 (s, 1H), 7.58 (s, 1H), 7.57 (s, 1H), 7.53 (s, 1H), 7.52 (s, 1H), 7.48 (s, 1H), 7.35 (s, 1H), 7.21 (s, 1H), 7.19 (t, 1H, J = 7.8 Hz), 7.14 (s, 1H), 7.10 (s, 1H), 7.03 (s, 1H), 6.98 (s, 1H), 6.70 (s, 1H), 6.61 (d, 1H, J = 7.7 Hz), 6.16 (t, 1H, J = 8.1 Hz), 6.14 (t, 1H, J = 8.1 Hz), 6.10 (t, 1H, J = 8.1 Hz), 6.04 (t, 1H, J = 8.2 Hz), 4.66 (d, 1H, J = 13.0 Hz), 4.32 (d, 1H, J = 13.2 Hz), 3.03-3.00 (m, 1H), 2.94-2.90 (m, 1H), 2.68-2.37 (m, 12H), 1.76-1.70 (m, 1H), 1.67-1.61 (m, 1H), 1.51-1.30 (m, 80H), 1.42 (t, 3H, J = 7.6 Hz), 1.29 (t, 3H, J = 7.7 Hz), 1.10 (t, 3H, J = 7.6 Hz), 1.06 (t, 3H, J = 7.5 Hz), 0.99 (t, 12H, J = 7.6 Hz), 0.97 (t, 3H, J = 7.5 Hz), 0.51 (t, 3H, J = 7.7 Hz), 0.03 (bs, 1H), -0.25 (bs, 1H), -0.89 (bs, 1H), -1.08 (bs, 1H), -1.20 (bs, 1H), -1.97 (bs, 2H), -2.66--2.76 (m, 3H), -2.86--2.94 (m, 2H), -2.98--3.02 (m, 1H).
HR ESI-MS m/z = 2176.3142 (calculated 2176.3232 for $C_{135}H_{174}N_{10}O_{15}+H^+$).

^{1}H-NMR spectrum of the Ouroborand **9**, in mesitylene d^{12} :