Supplementary Material (ESI) for Chemical Communications

Dynamic Combinatorial Olefin Metathesis: Templated Synthesis of Covalent Porphyrin Boxes

Supporting Information

General

All synthetic manipulations were carried out under a dry argon or nitrogen atmosphere using standard Schlenk techniques. Solvents were degassed by repeated freeze-thaw-pump cycles prior to synthesis. ^{1}H NMR spectra were recorded on a Varian Inova Unity 400 spectrometer and chemical shifts are reported relative to TMS (δ 0.00 ppm). UV-VIS spectra were recorded on a Varian Cary 50 Conc spectrophotometer. MALDI-TOF MS was carried out on a Bruker MALDI-TOF BIFLEX mass spectrometer. The samples were prepared by premixing 10 µl of a concentrated solution of analyte in $CHCl_3$ with 10 µl solution of dithranol in $CHCl_3$ (10 mg/ml) and applying 1 µl of this mixture on the sample plate for analysis.

Materials

Anhydrous dichloromethane, first and second generation Grubbs' catalyst and tetrapyridyl porphyrin were obtained from Aldrich and used as received. Porphyrin **Zn1** was synthesized by condensation of toluyldipyrromethane and 4-pent-4-enyloxy-benzaldehyde under Lindsey low scrambling conditions.[1] Size exclusion chromatography was performed with Bio-Rad S-X1 Beads (200-400 Mesh) eluted with distilled dichloromethane.

Synthesis of Zn4.TPyP (route A)

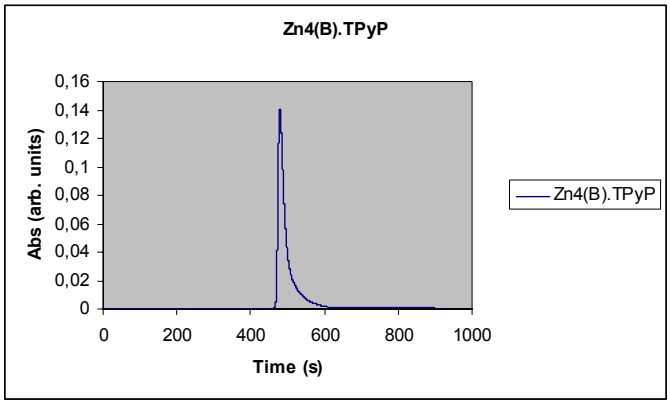
Zn1 (26.49 mg, 0.030 mmol) and 4.62 mg (7.47 µmol) of **TPyP** in 18 ml CH_2Cl_2 were briefly sonicated and subsequently stirred for 45 minutes. Next, a solution of 12.70 mg (0.015 mmol) of **Ru3** in 3 ml of CH_2Cl_2 was added through a canula, and the mixture was stirred for 12 hrs,[2] during the first 6 of which a gentle flow of argon was allowed to pass over the reaction mixture to remove any gaseous byproducts. The mixture was concentrated on a rotary evaporator and the resulting purple solid was redissolved as much as possible in 15 ml of CH_2Cl_2. Insoluble material was disposed off by centrifugation after which the supernatant was collected, filtered over cotton wool and purified by size exclusion chromatography (Bio-Beads). The cyclic tetramer was collected from a red band, although MALDI-TOF MS showed the presence of several other oligomers. The yield of this mixture was 8.5 mg (< 28 % cyclic tetramer).

Synthesis of Zn4.TPyP (route B)

In a typical procedure, 30.17 mg (0.035 mmol) of **Zn1** was dissolved in 20 ml of CH_2Cl_2. A solution of 2.31 mg (2.81 µmol) of **Ru2** in 2 ml of CH_2Cl_2 was added through a canula and the resulting mixture was refluxed for 12 hrs. Next, **TPyP** (5.22 mg, 8.44 µmol) was added while the solution was allowed to cool to room temperature and then stirred for an additional 30 min. Finally, 2.62 mg (3.09 µmol) of **Ru3** was added and the mixture was stirred for 6 hrs. After the mixture had been concentrated to 3 ml, as much solid as possible was redissolved with CH_2Cl_2. Insoluble material was disposed off by means of centrifugation after which the supernatant was collected. Volatiles were removed on a rotary evaporator and the obtained purple solid was redissolved in a minimal amount of CH_2Cl_2 and purified by chromatography over a Bio-Beads size exclusion column. The cyclic tetramer was collected from a dark purple band, which was chromatographed once again. Yield: 21.3 mg (62 %) of purple solid. ^{1}H NMR ($CDCl_3$, 400.15 MHz) δ 8.93 (br, 32 H, β-pyrrole H), 8.10 (br d, 16 H, $H_{2,4}$ -*Ph*OR), 8.05 (br d, 16 H, $H_{2,4}$ -*Ph*CH_3), 7.50 (br d, 16 H, $H_{3,5}$ –*Ph*CH_3), 7.28 (br d, 16 H, $H_{3,5}$ –*Ph*OR), 6.88 (br s, 8 H, β-pyrrole TPyP), 5.80 (br d, 8 H, Pyr H_β), 5.73 (br, 6 H, Z –CH=CH-), 5.67 (br t, 2 H, E –CH=CH-), 4.33 (br t, 16 H, H_α -PhO*R*), 2.71 (br s, 24 H -PhC*H*$_3$), 2.63 (br d, 8 H, Pyr H_α), 2.46 (m, 16H, H_γ -PhO*R*), 2.09 (m, 16H, H_β -PhO*R*), -4.71 (s, 2 H, N*H* TPyP) ppm. UV-VIS (CH_2Cl_2) λ_{max} (ε [10^4 cm^{-1} M^{-1}]): 603.0 (2.99), 563.0 (3.99), 522.5 (2.61), 426.0 (67.5) nm. MALDI-TOF observed M^+ 3377.63 amu, calculated for **Zn1b** 3377.10 amu .

GPC

Analysis of **Zn4.TPyP** (prepared by route B) was carried out on a Shimadzu LC 10-AD GPC Pump equipped with a Polymer Laboratories PLgel 5 µm MIXED-D column running on $CHCl_3$. For detection a Shimadzu SPD-10AV UV-VIS detector operating at 425 nm was used.



STM

STM measurements were carried out in the constant current mode using a home-built low-current STM. For each experiment the HOPG surface was freshly cleaved and the STM tips were mechanically cut from a Pt:Ir (80:20) wire. A drop of a nearly saturated solution of **Zn5.TPyP** in 1-phenyloctane/$CHCl_3$ (1:4, v/v) was brought onto the surface. Typically, an STM image (512 lines × 512 points) was recorded over a period of 10 min. Experiments were carried out in duplicate and the raw data were processed only by the application of a background flattening. Before and after the experiments the piezo element was calibrated *in situ* by lowering the bias voltage to 100 mV and raising the tunneling current to 50 pA, which allowed imaging of the HOPG surface underneath the molecules.

References and notes

1. Littler, B.J.; Ciringh, Y.; Lindsey, J.S. *J. Org. Chem.* **1999**, *64*, 2864
2. Adding another 0.5 equivalent of catalyst after 12 hrs did not significantly enhance the yield of cyclic tetramer