Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Porphyrin based molecular turnstiles

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Experimental Section

Dipyrromethane **18**[1] and 3-(cyclohexyl)phenol[2] were synthesized according to published procedures. CH_3CN, $CHCl_3$ and DMF were dried over molecular sieves; THF and CH_2Cl_2 were dried and distilled over sodium and CaH_2, respectively. Triethylamine was dried and distilled over KOH. Analytical ethanol, methanol and pyridine were used without further purification.

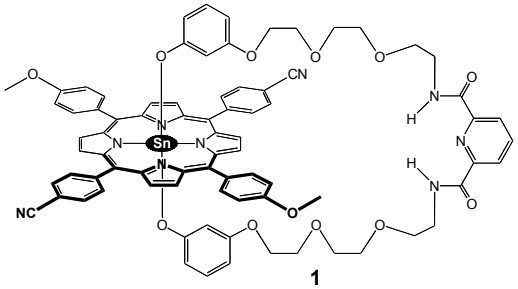
^1H and ^{13}C-NMR spectra were recorded at 25°C unless stated otherwise on either a Bruker AV 300 (300 MHz), Bruker AV 400 (400 MHz) or a Bruker AV 500 (500 MHz) spectrometer, with the deuterated solvent as the lock and residual solvent as the internal reference. Absorption spectra were recorded using an Uvikon XL spectrophotometer. Elemental analyses were performed by the Service de Microanalyses, UdS, Strasbourg, mass spectrometry analyses were performed by the Service de Spectrometrie de Masse, UdS, Strasbourg. Melting points were measured using a Stuart Scientific Melting Point SMP-1 apparatus without further correction.

X-ray structural determination

Data for **2** were collected on a Bruker SMART CCD diffractometer with Mo–Kα radiation. The structure was solved using SHELXS-97 and refined by full matrix least-squares on F^2 using SHELXL-97 with anisotropic thermal parameters for all non hydrogen atoms. The hydrogen atoms were introduced at calculated positions and not refined (riding model).

CCDC 759474 contains the supplementary crystallographic data for compounds **2**. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif.

Synthesis



1

In a dry 100 mL round-bottom flask, compound **21** (15 mg, 0.02 mmol, 1 eq.) and **14** (11 mg, 0.02 mmol, 1 eq.) were dissolved in 30 mL of CH_2Cl_2. The reaction mixture was stirred at room temperature and under argon for 15 days. The solvent was evaporated to dryness and the residue was crystallised from a toluene/pentane mixture (1/2, 30 mL) to yield the desired complex (**1**) (22 mg, 86%) as a purple-green solid.

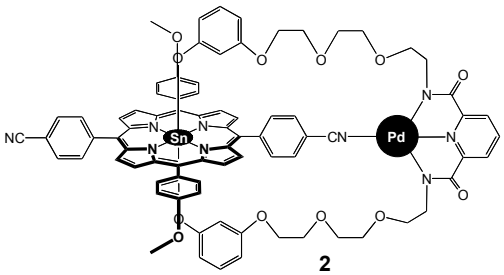
IR (KBr, cm^{-1}): 3337 (NH amide), 2225 (CN), 1671 (CO amide).

UV (CH_2Cl_2, λ_{max} (log ε)): 432 (5.5), 564 (4.3), 606 (4.1).

^{1}H-NMR (CD_2Cl_2, 500 MHz) δ (ppm): 1.27 (t, 2H, Ar_h, ^4J = 2.5 Hz), 1.53 (dd, 2H, Ar_i, ^3J = 7.5 Hz, ^4J = 2.0 Hz), 3.22-3.26 (m, 4H, $OCH_{2\ l}$), 3.49-3.53 (m, 4H, $OCH_{2\ m}$), 3.66-3.71 (m, 4H, $OCH_{2\ n}$), 3.76-3.80 (m, 4H, $OCH_{2\ o}$), 3.82-3.89 (m, 8H, $NCH_{2\ q}$, $OCH_{3\ p}$), 4.16 (s, 6H, $OCH_{3\ g}$), Ar_k overlapped by CH_2Cl_2, 5.54 (t, 2H, Ar_j, ^3J = 8.0 Hz), 7.44 (dd, 4H, Ar_f, ^3J = 6.5 Hz, ^4J = 2.0 Hz), 8.10 (t, 1H, Py_s, ^3J = 8.0 Hz), 8.22 (dd, 4H, Ar_e, ^3J = 6.5 Hz, ^4J = 2.0 Hz), 8.27 (dd, 4H, Ar_a, ^3J = 6.5 Hz, ^4J = 2.0 Hz), 8.38 (d, 2H, Py_r, ^3J = 8.0 Hz), 8.41 (dd, 4H, Ar_b, ^3J = 6.5 Hz, ^4J = 2.0 Hz), 8.76 (t, 2H, NH_t, ^3J = 6.0 Hz), 9.05 (d, 4H, β-$pyr._c$, ^3J = 5.0 Hz, J_{Sn-H} = 17.0 Hz), 9.27 (d, 4H, β-$pyr._d$, ^3J = 5.0 Hz, J_{Sn-H} = 16.5 Hz).

^{13}C-NMR (CD_2Cl_2, 125 MHz) δ (ppm): 39.9, 56.1, 66.6, 70.1, 70.2, 70.7, 71.0, 102.9, 103.8, 110.9, 113.2, 125.0, 126.8, 131.5, 132.2, 133.3, 133.7, 135.7, 136.5, 139.3, 146.0, 146.9, 148.2, 149.5, 156.4, 157.5, 160.6, 164.2.

MS (ESI) for **1** ($C_{79}H_{67}N_9O_{12}Sn$: 1453.14 $g.mol^{-1}$): *m/z* 1460.41 ($M+Li^+$).



2

In a dry 50 mL two-necked round-bottom flask, compound **21** (23 mg, 0.03 mmol, 1 eq.) was introduced. A solution of palladium complex **15** (20 mg, 0.03 mmol, 1 eq.) in 15 mL of CH_2Cl_2 was added under argon. The reaction mixture was stirred at room temperature under argon for 2 days. The solvent was evaporated to dryness and the residue was crystallised from a toluene/pentane mixture (1/2, 45 mL) to yield the desired complex **2** (34 mg, 83%) as a green solid.

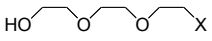
IR (ATR, cm^{-1}): 2273 (CN···Pd), 2227 (CN).

UV (CH_2Cl_2, λ_{max} (log ε)): 432 (5.4), 565 (4.3), 607 (4.3).

^{1}H-NMR (CD_2Cl_2, 500 MHz) δ (ppm): 1.30 (t, 2H, Ar_h, ^4J = 2.5 Hz), 1.53 (ddd, 2H, Ar_i, ^3J = 8.0 Hz, ^4J = 2.0 Hz, ^4J = 0.5 Hz), 3.31-3.38 (m, 4H, $OCH_{2\ l}$), 3.49-3.54 (m, 4H, $OCH_{2\ m}$), 3.66-3.71 (m, 4H, $OCH_{2\ n}$), 3.78-3.82 (m, 8H, $OCH_{2\ p}$, $NCH_{2\ q}$), 3.82-3.86 (m, 4H, $OCH_{2\ o}$), 4.13 (s, 6H, $OCH_{3\ g}$), 5.27 (ddd, 2H, Ar_k, ^3J = 8.0 Hz, ^4J = 2.5 Hz, ^4J = 0.5 Hz), 5.51 (t, 2H, Ar_j, ^3J = 8.0 Hz), 7.40 (dd, 4H, Ar_f, ^3J = 6.5 Hz, ^4J = 2.0 Hz), 7.71 (d, 2H, Py_r, ^3J = 8.0 Hz), 8.09 (t, 1H, Py_s, ^3J = 8.0 Hz), 8.19 (dd, 2H, Ar_a, ^3J = 6.5 Hz, ^4J = 2.0 Hz), 8.22 (dd, 4H, Ar_e, ^3J = 6.5 Hz, ^4J = 2.0 Hz), 8.40 (dd, 2H, $Ar_{b'}$, ^3J = 6.5 Hz, ^4J = 2.0 Hz), 8.46 (dd, 2H, $Ar_{a'}$, ^3J = 6.5 Hz, ^4J = 1.5 Hz), 8.57 (dd, 2H, Ar_b, ^3J = 6.5 Hz, ^4J = 2.0 Hz), 8.71 (d, 2H, β-$pyr._{c'}$, ^3J = 5.0 Hz, J_{Sn-H} = 17.0 Hz), 9.10 (d, 2H, β-$pyr._{d'}$, ^3J = 5.0 Hz, J_{Sn-H} = 16.5 Hz), 9.23 (d, 2H, β-$pyr._c$, ^3J = 5.0 Hz, J_{Sn-H} = 17.5 Hz), 9.37 (d, 2H, β-$pyr._d$, ^3J = 5.0 Hz, J_{Sn-H} = 17.5 Hz).

^{13}C-NMR (CD_2Cl_2, 125 MHz) δ(ppm): 46.5, 56.1, 66.7, 71.0, 71.3, 71.3, 71.8, 101.8, 104.3, 108.6, 111.4, 113.2, 119.2, 119.4, 120.4, 123.0, 123.8, 125.0, 126.8, 131.5, 131.5, 132.7, 133.0, 133.2, 133.6, 134.0, 135.7, 136.0, 136.5, 141.6, 146.0, 146.7, 147.0, 148.3, 148.4, 148.6, 153.5, 156.9, 157.4, 160.7, 170.8.

MS (ESI) for **2** ($C_{79}H_{65}N_9O_{12}PdSn$: 1557.54 g.mol^{-1}): *m/z* 1558.29 ($M+H^+$).



4 X = NPhth

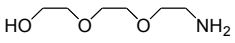
To a solution of 2-[2-(2-chloroethoxy)ethoxy]ethanol (10.32 g, 61.2 mmol, 1 eq) in 100 mL of dry DMF was added under argon freshly prepared potassium phthalimide (12.6 g, 68.0 mmol, 1.1 eq). The resulting solution was heated at 110°C for 6 h to afford a yellow suspension. The mixture was cooled in an ice-water bath and the precipitate was filtered and washed with 100 mL of Et_2O. The combined filtrates were stored at RT overnight and the resulting precipitate was filtered off. The solution was evaporated to dryness to afford a yellow oil which was purified by chromatography (SiO_2, ethyl acetate). The resulting colourless oil was dried under vacuum for 24 h to yield a white powder (13.6 g, 80%).[3]

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 2.41 (br s, 1H, OH), 3.51-3.53 (m, 2H, CH_2O), 3.57-3.66 (m, 6H, CH_2O), 3.74 (t, 2H, CH_2O, ^3J = 5.7 Hz), 3.90 (t, 2H, CH_2N, ^3J = 5.6 Hz), 7.70 (dd, 2H, CH_{Phth}, ^3J = 5.4 Hz, ^4J = 3.1 Hz), 7.84 (dd, 2H, CH_{Phth}, ^3J = 5.4 Hz, ^4J = 3.1 Hz).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 37.2, 61.8, 67.9, 70.0, 70.4, 72.4, 123.3, 132.1, 134.0, 168.4.

Anal. Calcd for **4**: C, 60.21%; H, 6.14%; N, 5.02%; Found: C, 60.48%; H, 6.33%; N, 4.95%.

Mp = 47-49°C.



5 X = NPhth

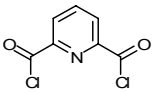
To a suspension of **4** (2.40 g, 8.6 mmol, 1 eq) in 30 mL of ethanol was added hydrated hydrazine (98%) (0.45 mL, 8.6 mmol, 1 eq). The resulting mixture was refluxed for 15 h. After cooling of the solution, 9 mL of a 1M HCl solution was added and the resulting solution was again refluxed for 4 h. After removal of the solvent, 50 mL of water was added to the solid yellow residue. After filtration of the precipitate, the aqueous layer was basified using 30 mL of a 10% aqueous NaOH solution until pH = 12 was reached before the mixture was evaporated to dryness. The residue was washed with CH_2Cl_2 and filtered. The oily residue was purified by distillation under reduced pressure to afford a colourless oil (0.82 g, 64%).[4]

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 2.86 (t, 2H, CH_2N, ^3J = 5.0 Hz), 3.51-3.70 (m, 10H, CH_2O).

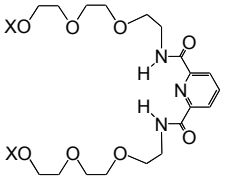
^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 41.4, 61.5, 70.1, 70.3, 72.7, 72.9.

Anal. Calcd for **5**·2.2H_2O: C, 38.14%; H, 10.28%; N, 7.41%; Found C, 38.26%; H, 10.51%; N=7.05%.

Pyridine 2,6-dicarbonyl chloride: **7**[5]



A suspension of pyridine-2,6-dicarboxylic acid (5.0 g, 30 mmol, 1 eq) in thionyl chloride (50 mL, 685 mmol, 23 eq) was refluxed under argon for 7 h. After evaporation to dryness, the solid residue was further dried under vacuum overnight. A white powder was obtained (6.1 g, 100%).



11 X = H

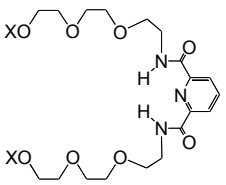
To a solution of **5** (1.17 g, 7.84 mmol, 2 eq) in 60 mL of distilled CH_2Cl_2 cooled to 0 °C was added under argon distilled triethylamine (1.2 mL, 8.84 mmol, 2.2 eq). Then, a solution of pyridine-2,6-dicarbonyl chloride **7** (0.80 g, 3.92 mmol, 1 eq) in 90 mL of distilled CH_2Cl_2 was added *via* a cannula at 0 °C. The resulting mixture was stirred at room temperature for 44 h.

After removal of the solvent, the residue was purified by chromatography (Al_2O_3, CH_2Cl_2/MeOH 0-10%) to afford a colourless oil (1.25 g, 75%).

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 3.59-3.74 (m, 24H, CH_2O and CH_2N), 7.98 (t, 1H, CH_{Py}, ^3J = 7.8 Hz), 8.30 (d, 2H, CH_{Py}, ^3J = 7.9 Hz), 9.11 (br s, 2H, NH).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 39.5, 61.4, 70.0, 70.2, 70.5, 72.7, 124.7, 138.6, 148.8, 164.1.

Anal. Calcd for **11**·$2H_2O$: C, 48.98%; H 7.52%; N, 9.02%; Found C, 49.05%; H, 7.23%; N, 9.00%.



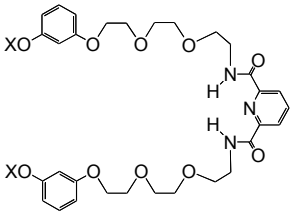
12 X = Ms

To a solution of **11** (0.80 g, 1.86 mmol, 1 eq) in 120 mL of distilled THF were added under argon successively distilled triethylamine (1.0 mL, 7.32 mmol, 3.9 eq) and a solution of methanesulfonyl chloride (0.5 mL, 6.21 mmol, 3.3 eq) in 60 mL of distilled THF *via* a cannula over 15 minutes. The resulting mixture was stirred at room temperature for 45 h. After removal of the solvent, the residue was dissolved in 170 mL of CH_2Cl_2 and washed with water (3x130 mL). The organic layer was dried over $MgSO_4$, filtered and evaporated. The oily residue was purified by chromatography (Al_2O_3, CH_2Cl_2/MeOH 0-10%) to afford colourless oil (0.80 g, 74%).

^{1}H-NMR ($CDCl_3$, 300MHz) δ (ppm): 3.04 (s, 6H, SO_2CH_3), 3.65-3.76 (m, 20H, CH_2O, CH_2N), 4.33-4.36 (m, 4H, CH_2O), 8.01 (t, 1H, CH_{Py}, ^3J = 7.8 Hz), 8.33 (d, 2H, CH_{Py}, ^3J = 7.8 Hz), 8.52 (br s, 2H, NH).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 37.6, 39.4, 68.9, 69.0, 70.0, 70.5, 124.9, 138.8, 148.8, 163.8.

Anal. Calcd for **12**·H_2O: C, 41.75%; H, 6.13%; N, 6.96%; Found: C, 41.72%; H, 6.21%; N, 7.12%.



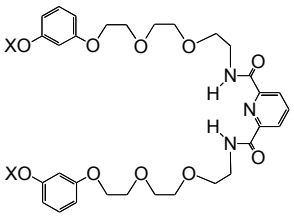
13 X = THP

To a degassed solution of 3-(cyclohexyloxy)phenol (438 mg, 2.26 mmol, 2.3 eq) in 60 mL of anhydrous CH_3CN was added under argon caesium carbonate (810 mg, 2.30 mmol, 2.4 eq). The mixture was stirred at room temperature for 3.5 hours to afford a white suspension. A solution of **12** (566 mg, 0.97 mmol, 1 eq) in 75 mL of anhydrous CH_3CN was then added *via* a cannula during 30 minutes. The resulting mixture was refluxed for 65 h. After filtration and removal of the solvent, the residue was dissolved in 150 mL of CH_2Cl_2 and washed with water (3x100 mL) and brine (150 mL). The organic layer was dried over $MgSO_4$, filtered and evaporated to dryness. The oily residue was purified by chromatography (Al_2O_3, CH_2Cl_2/MeOH 0-3%) to afford colourless oil (478 mg, 63%).

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 1.56-2.03 (m, 12H, CH_{2THP}), 3.55-4.08 (m, 24H, CH_2O, CH_2N), 5.36 (t, 2H, CH_{THP}, ^3J = 3.2 Hz), 6.47 (ddd, 2H, CH_{res}, ^3J = 8.4 Hz, ^4J = 2.4 Hz, ^4J = 0.8 Hz), 6.57 (t, 2H, CH_{res}, ^3J = 2.3 Hz), 6.63 (ddd, 2H, CH_{res}, ^3J = 8.3 Hz, ^4J = 2.3 Hz, ^4J = 0.7 Hz), 7.11 (t, 2H, CH_{res}, ^3J = 8.3 Hz), 7.96 (t, 1H, CH_{Py}, ^3J = 7.8 Hz), 8.29 (d, 2H, CH_{Py}, ^3J = 7.8 Hz), 8.62 (br s, 2H, NH).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 18.8, 25.2, 30.3, 39.5, 62.0, 67.2, 69.6, 70.0, 70.1, 70.7, 96.4, 103.3, 107.6, 109.0, 124.8, 129.7, 138.6, 148.8, 158.2, 159.6, 163.8.

Anal. Calcd for **13**·H_2O: C, 61.51%; H, 7.26%; N, 5.25%; Found: C, 61.85%; H, 7.60%; N, 5.21%.



14 X = H

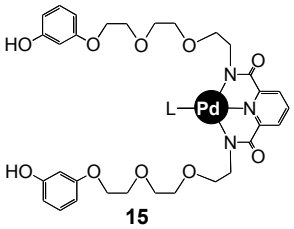
A solution of **13** (392 mg, 0.50 mmol) in 80 mL of CH_3OH in the presence of 1 mL of aqueous hydrochloric acid (37%) was stirred at room temperature for 3 h. The resulting solution was then basified with solid $NaHCO_3$ until pH = 7 was reached. After removal of the

solvent, the white residue was extracted using a Soxlhet apparatus and Et_2O (300 mL) for 3.5 days. After removal of Et_2O, a colourless oil was obtained (188 mg, 61 %).

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 3.62-3.79 (m, 20H, CH_2O, CH_2N), 3.97-4.01 (m, 4H, CH_2O), 6.34 (dd, 2H, CH_{res}, ^3J = 8.1 Hz ,^4J = 2.1 Hz), 6.40 (t, 2H, CH_{res}, ^4J = 2.3 Hz), 6.45 (dd, 2H, CH_{res}, ^3J = 8.1 Hz ,^4J = 2.0 Hz), 7.02 (t, 2H, CH_{res}, ^3J = 8.1 Hz), 7.95 (t, 1H, CH_{Py}, ^3J = 7.8 Hz), 8.28 (d, 2H, CH_{Py}, ^3J = 7.8 Hz), 9.00 (br s, 2H, NH).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 39.6, 67.0, 69.6, 69.8, 69.9, 70.5, 102.7, 106.3, 108.7, 125.0, 130.1, 138.9, 148.7, 157.4, 159.6, 164.4.

Anal. Calcd for **14**·0.5H_2O: C, 59.74%; H, 6.42%; N, 6.75%; Found: C, 59.77%; H, 6.32%; N, 6.35%.

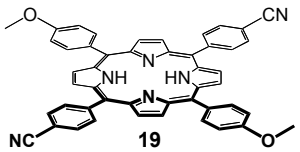


15

Palladium acetate (16 mg, 71 μmol 1.45 eq) was added to a solution of **14** (30 mg, 49 μmol, 1 eq) in 25 mL of dry CH_3CN under argon. The resulting solution was stirred at room temperature for 18 h. After removal of the solvent, the residue was taken up in hot CH_3CN, filtered and evaporated to afford an unstable yellow oil (30 mg, 80%).

^{1}H-NMR (CD_3CN, 300MHz) δ (ppm): 3.44 (m, 4H, CH_2), 3.54-3.64 (m, 12H, CH_2), 3.75 (m, 4H, CH_2), 4.00 (m, 4H, CH_2), 6.33-6.39 (m, 4H, Ar), 7.06 (t, 2H, Ar, ^3J = 8.0 Hz), 7.57 (d, 2H, Py, ^3J = 8.0 Hz), 7.67 (br s, 2H, OH), 8.07 (t, 1H, Py, ^3J = 8.0 Hz).

^{13}C-NMR (CD_3CN, 75 MHz) δ (ppm): 47.0, 68.4, 70.3, 71.2, 71.3, 71.5, 102.8, 107.0, 108.9, 125.4, 131.1, 153.8, 159.3, 172.7.



19

In a 250 mL two-necked round-bottom flask, compound **18** (2.0 g, 8.1 mmol, 1 eq.) was dissolved in 150 mL of a CH_2Cl_2/EtOH mixture (95/5). To the solution, compound **17** (1.0 mL, 8.2 mmol, 1 eq.) was added and the mixture was degassed using argon for 5 min. Under argon and in exclusion of light, TFA (1.2 mL, 16.2 mmol, 2 eq.) was added and the solution

stirred at room temperature for 2 days before triethylamine (3.8 mL) was added to neutralize the excess of TFA. A solution of DDQ (2.7 g, 11.9 mmol, 1.5 eq) in 100 mL of THF was added and the mixture was stirred at room temperature for 1 day. The crude product was purified by chromatography (SiO_2, CH_2Cl_2/cyclohexane, 2/3-1/0), to yield the desired product **19** (361 mg, 12%) as a purple solid.[6]

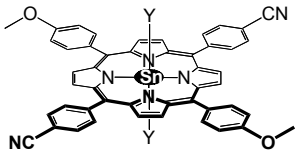
IR (KBr, cm^{-1}): 3321 (NH), 3291 (NH), 2222 (CN).

UV (CH_2Cl_2, λ_{max} (log ε)): 421 (5.6), 517 (4.2), 554 (3.9), 592 (3.7), 648 (3.6).

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): -2.82 (br s, 2H, NH), 4.11 (s, 6H, OCH_3), 7.31 (dd, 4H, Ar, ^{3}J = 6.5 Hz, ^{4}J = 2.0 Hz), 8.08 (dd, 4H, Ar, ^{3}J = 6.5 Hz, ^{4}J = 1.5 Hz), 8.11 (dd, 4H, Ar, ^{3}J = 6.5 Hz, ^{4}J = 2.0 Hz), 8.34 (dd, 4H, Ar, ^{3}J = 6.5 Hz, ^{4}J = 2.0 Hz), 8.73 (d, 4H, β-pyr., ^{3}J = 5.0 Hz), 8.92 (d, 4H, β-pyr., ^{3}J = 5.0 Hz).

^{13}C-NMR ($CDCl_3$, 125 MHz) δ (ppm): 55.7, 112.4, 113.7, 118.2, 119.2, 120.7, 130.8, 134.1, 135.2, 136.0, 139.0, 147.3, 159.9.

Anal. Calcd for **19** $0.5H_2O$ $0.5CH_2Cl_2$ $0.5C_6H_{12}$: C, 75.58%; H, 4.93%; N, 10.27%; Found: C, 75.76%; H, 4.91%; N, 10.26.



20 Y = Cl

In a 100 mL round-bottom flask, compound **19** (170 mg, 0.2 mmol, 1 eq.) was dissolved in 40 mL of pyridine. To the solution, $SnCl_2 \cdot 2H_2O$ (159 mg, 0.7 mmol, 3 eq.) was added and the mixture was refluxed over night. The solvent was evaporated to dryness and the residue dissolved in CH_2Cl_2 was filtered over celite to yield the desired product **20** (211 mg, 99%) as a purple solid.[7]

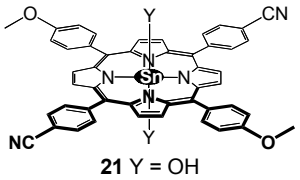
IR (KBr, cm^{-1}): 2229 (CN).

UV (CH_2Cl_2, λ_{max} (log ε)): 432 (5.5), 563 (4.3), 606 (4.1).

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 4.13 (s, 6H, OCH_3), 7.37 (d, 4H, Ar, ^{3}J = 8.5 Hz), 8.15 (d, 4H, Ar, ^{3}J = 8.0 Hz), 8.22 (d, 4H, Ar, ^{3}J = 8.5 Hz), 8.46 (d, 4H, Ar, ^{3}J = 8.0 Hz), 9.15-9.07 (m, 4H, β-pyr.), 9.26-9.35 (m, 4H, β-pyr.).

^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 55.6, 112.7, 112.7, 118.4, 121.8, 130.9, 131.6, 132.1, 133.4, 135.1, 136.0, 144.9, 145.3, 147.0, 160.1.

Anal. Calcd for **20** $0.3C_6H_{12}$: C, 63.86%; H, 3.64%; N, 8.94%; Found: C, 64.05%; H 3.79%; N, 8.92%.



21 Y = OH

In a 250 mL round-bottom flask, compound **20** (149 mg, 0.2 mmol, 1 eq.) was dissolved in 75 mL of a CH_2Cl_2/MeOH (4/1) mixture before solid K_2CO_3 (1.0 g, 7.2 mmol, 44 eq.) was added and the solution refluxed for 4 hours. The organic layer was washed with distilled water (3x50 mL) and dried over $MgSO_4$. After removal of the solvent under vacuum, the residue was purified on a chromatography column (Al_2O_3, $CHCl_3$) to yield the desired product **21** (119 mg, 83%) as a purple solid.[8]

IR (KBr, cm^{-1}): 3641 (OH), 2227 (CN).

UV (CH_2Cl_2, λ_{max} (log ε)): 432 (5.7), 565 (4.3), 606 (4.2).

^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): -7.44 (br s, 2H, OH), 4.13 (s, 6H, OCH_3), 7.37 (d, 4H, Ar, ^3J = 9.0 Hz), 8.15 (d, 4H, Ar, ^3J = 8.5 Hz), 8.24 (d, 4H, Ar, ^3J = 9.0 Hz), 8.47 (d, 4H, Ar, ^3J = 8.5 Hz), 9.03 (d, 4H, β-pyr., ^3J = 5.0 Hz, J_{Sn-H} = 15.5 Hz), 9.22 (d, 4H, β-pyr., ^3J = 5.0 Hz, J_{Sn-H} = 15.5 Hz).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 55.7, 112.6, 112.8, 118.8, 122.2, 130.9, 132.0, 133.1, 133.6, 135.4, 136.3, 145.9, 146.0, 147.4, 160.1.

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