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Electronic Supplementary Informations

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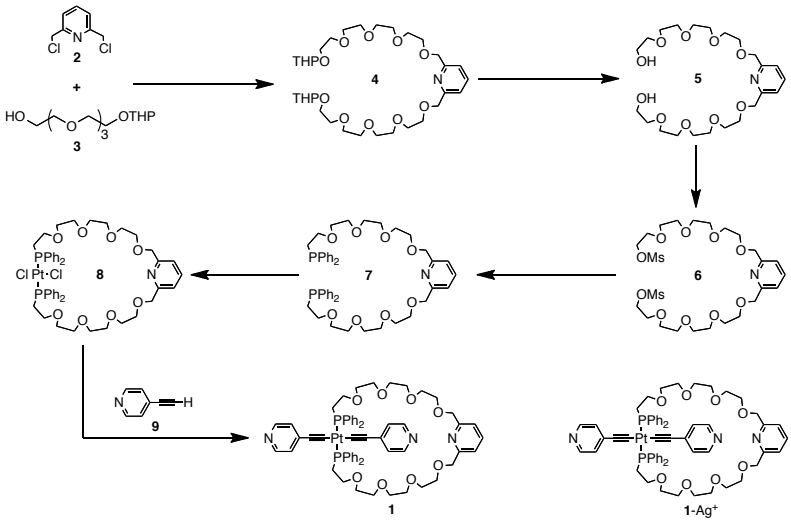
Experimental section



THF, CH_2Cl_2 and triethylamine were distilled over sodium, CaH_2 and KOH, respectively. Analytical grade MeOH, toluene and CH_3CN were used without further purification. ^{1}H- ^{31}P- and ^{13}C-NMR spectra were acquired at 25°C on either Bruker AV 300, Brucker AV 400, Brucker AV 500, or Brucker AV 600 spectrometers in deuterated solvents and residual solvent peak was used as the internal reference. Absorption spectra were recorded on an Uvikon XL spectrophotometer. MS was performed by the Service de Spectrometrie de Masse, University of Strasbourg.
2,6-bis(chloromethyl)pyridine **2**,[1,2] 4-ethynylpyridine **9**[3] and 2-(2-(2-(2-((tetrahydro-2H-pyran-2-yl)oxy)ethoxy)ethoxy)ethoxy)ethanol **3**[4] were synthesized according to published procedures.

2,6-bis(13-((tetrahydro-2H-pyran-2-yl)oxy)-2,5,8,11-tetraoxatridecyl)pyridine 4: A solution of compound **3** (6.12 g, 22 mmol, 2.2 eq.) in dry THF (50 mL) was added dropwise over 30 min to a suspension of NaH (60 % in oil, 0.875 g, 22 mmol, 2.2 eq.) in dry THF (150 mL). After 40 min, a solution of compound **2** (1,75 g, 10 mmol, 1 eq.) in dry THF (90 mL) was added over a period of one hour. The reaction mixture was then refluxed for 5 days. After evaporation of the solvent, the resulting oil was dissolved in CH_2Cl_2 (200 mL), washed with distilled water (3x200 mL) and brine (100 mL). The organic layer was dried over $MgSO_4$, evaporated and purified by column chromatography (Al_2O_3, petroleum ether/EtOAc 1:1 to 3:7) to yield compound **4** (3.9 g, 59 %) as a yellow oil.

^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) = 1.47-1.87 (m, 12H, CH_2), 3.45-3.90 (m, 36H, OCH_2), 4.62 (m, 2H, CH), 4.68 (s, 4H, OCH_2), 7.39 (d, 2H, ^3J = 8.0 Hz), 7.72 (t, 1H, ^3J = 8.0 Hz)

^{13}C-NMR ($CDCl_3$, 75 MHz): δ (ppm) = 19.6, 25.6, 30.7, 62.4, 66.8, 70.4, 70.7, 70.8, 70.8, 74.0, 99.1, 120.1, 137.5, 157.9

Elemental analysis calcd (%) for $C_{33}H_{57}NO_{12}$: C 60.07 H 8.71 N 2.12; found: C 59.95 H 9.07 N 1.88

1,1'-(pyridine-2,6-diyl)bis(2,5,8,11-tetraoxatridecan-13-ol) 5: 2.6 mL of a 37 % HCl aqueous solution were added dropwise to a solution of compound **4** (3.9 g, 5.9 mmol, 1 eq.) in MeOH (300 mL). The resulting solution was stirred at RT for one day. $NaHCO_3$ was then added until pH 7 was reached. After evaporation of the solvent, the resulting solid was suspended in Et_2O (500 mL), filtrated on a sintered glass-funnel, and evaporated to dryness to afford **5** (2.6 g, 90 %) as a yellow oil.

^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) = 2.83 (br, 2H, OH), 3.58-3.75 (m, 32H, OCH_2), 4.67 (s, 4H, OCH_2), 7.38 (d, 2H, ^3J = 8.0 Hz), 7.72 (t, 1H, ^3J = 8.0 Hz)

^{13}C-NMR ($CDCl_3$, 75 MHz): δ (ppm) = 61.8, 70.4, 70.5, 70.7, 70.8, 72.7, 74.0, 120.2, 137.6, 157.9

Elemental analysis calcd (%) for $C_{23}H_{41}NO_{10}$·0.5 $C_4H_{10}O$: C 56.80 H 8.77 N 2.65; found: C 56.79 H 8.70 N 2.62

1,1'-(pyridine-2,6-diyl)bis(2,5,8,11-tetraoxatridecane-13,1-diyl) dimethanesulfonate 6: To a solution of compound **5** (2.37 g, 4.8 mmol, 1 eq.) in dry THF (100 mL) were added successively freshly distilled NEt_3 (2.3 mL, 16 mmol, 3.4 eq.) and MsCl (1.1 mL, 15 mmol, 3 eq.). The reaction mixture was stirred at RT for 5 hours. After evaporation under reduced pressure, the white solid was dissolved in CH_2Cl_2 (100 mL), washed with water (3x75 mL), and a 5% aqueous $NaHCO_3$ solution (3x75 mL). The organic layer was dried over $MgSO_4$ and evaporated to dryness to give compound **6** (3.11 g, quant.) as a slightly yellow oil.

^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) = 3.06 (s, 6H, CH3), 3.62-3.77 (m, 28H, OCH_2), 4.36 (m, 4H, OCH_2), 4.68 (s, 4H, OCH_2), 7.39 (d, 2H, ^3J = 8.0 Hz), 7.73 (t, 1H, ^3J = 8.0 Hz)

^{13}C-NMR ($CDCl_3$, 75 MHz): δ (ppm) = 37.9, 69.1, 69.4, 70.4, 70.7, 70.8, 73.9, 120.3, 137.8, 157.8

Elemental analysis calcd (%) for $C_{25}H_{45}NO_{14}S_2$: C 46.36 H 7.00 N 2.16; found: C 46.35 H 6.87 N 2.05

2,6-bis(13-(diphenylphosphino)-2,5,8,11-tetraoxatridecyl)pyridine 7: Under an argon atmosphere, to a solution of compound **6** (503 mg, 0.78 mmol, 1 eq.) in dry THF (25 mL) cooled to 0 °C, a 0.5 M solution of $KPPh_2$ in THF (3.2 mL, 1.6 mmol, 2.06 eq) was added dropwise. The reaction mixture was then allowed to reach RT and stirred for 4 hours. After removal of the solvent, the crude product was partially dissolved in CH_2Cl_2 (50 mL), filtrated over a sintered-glass funnel, and evaporated to dryness. The product was purified by column chromatography (Al_2O_3, CH_2Cl_2/MeOH 100:0 to 99:1) to yield compound **7** (454 mg, 71%) as a pale yellow oil.

^{1}H-NMR (CD_2Cl_2, 300 MHz): δ (ppm) = 2.38 (t, 4H, PCH_2, J = 7.4 Hz), 3.48-3.71 (m, 28H, OCH_2), 4.60 (s, 4H, OCH_2), 7.29-7.46 (m, 22H, Ph + pyr), 7.69 (t, 1H, ^3J = 7.7 Hz)

^{13}C-NMR (CD_2Cl_2, 75 MHz): δ (ppm) = 29.2, 68.6, 68.9, 70.5, 70.7, 70.9, 70.9, 71.0, 74.4, 120.2, 128.7, 128.8, 128.9, 132.9, 133.1, 158.4.

^{31}P-NMR (CD_2Cl_2, 121.5 MHz): δ (ppm) = -22.2

Elemental analysis calcd (%) for $C_{47}H_{59}NO_8P_2$: C 68.18 H 7.18 N 1.69; found: C 68.30 H 7.00 N 1.635

Compound 8: Two solutions of compound **7** (128.8 mg, 0.155 mmol, 1 eq.) and $CODPtCl_2$ (59.0 mg, 0.157 mmol, 1 eq.) in dry and degassed CH_2Cl_2 (50 mL each) were prepared separately. The two solutions were added simultaneously using syringe pumps (3 mL/hour) to a dry, degassed CH_2Cl_2 (200 mL) contained in a dry 1 L three-necked round-bottomed flask. The resulting mixture was then stirred overnight. After removal of the solvent under reduced pressure, the product was purified by column chromatography (Al_2O_3, EtOAc) to yield **8** (105 mg, 62 %) as a pale yellow solid.

^{1}H-NMR (CD_2Cl_2, 300 MHz): δ (ppm) = 2.40 (br, 4H, PCH_2), 3.36-3.77 (m, 28H, OCH_2), 4.61 (s, 4H, OCH_2), 7.23-7.56 (m, 22H, Ph + pyr), 7.66 (t, 1H, pyr, ^3J = 7.6 Hz).

^{13}C-NMR ($CDCl_3$, 125 MHz): δ (ppm) = 30.6, 67.0, 70.0, 70.3, 70.4, 70.6, 70.6, 70.7, 74.1, 120.1, 128.4, 131.1, 133.5, 137.4, 157.9.

^{31}P-NMR ($CDCl_3$, 162 MHz): δ (ppm) = 5.0 ($J_{P\text{-}Pt}$ = 1818 Hz)

UV-Vis (CH_2Cl_2) λ_{max} (nm) (ε, $mol^{-1}\cdot L\cdot cm^{-1}$): 230 ($1.8\cdot10^4$), 270 ($9.7\cdot10^3$)

MS (ESI): m/z calcd for $C_{47}H_{59}NO_8P_2PtCl^+$: 1058.305 g·mol^{-1}; found: 1058.326 g·mol^{-1}

Compound 1: Compound **8** (100 mg, 0.091 mmol, 1eq.) and 4-ethynylpyridine **9** (47 mg, 0.46 mmol, 5 eq.) were dissolved in a degassed toluene:CH_2Cl_2 1:1 mixture (12 mL). NEt_3 (2.5 mL) was added and the reaction mixture was degassed by freeze-thaw cycles. After one cycle, CuI (3 mg, 0.013 mmol, 0.15 eq.) was added to the cold mixture. After 5 more cycles, the reaction mixture was allowed to slowly reach RT and stirred for 5 days. After filtration on Celite and evaporation of the filtrate, the product was purified by column chromatography (SiO_2, $CHCl_3$/MeOH 9:1) and then by Sephadex LH-20 columns using CH_2Cl_2/MeOH 7/3 as the eluant (the process was repeated several times) to afford the desired product as a yellow solid (44 mg, 39 %).

^{1}H-NMR (CD_2Cl_2, 500 MHz): δ (ppm) = 3.15 (br, 4H, H_l), 3.46 (m, 8H, H_{i-j}), 3.51 (m, 4H, H_h), 3.55 (m, 4H, H_g), 3.62 (m, 4H, H_f), 3.67 (m, 4H, H_e), 3.90 (m, 4H, H_k), 4.59 (s, 4H, H_d), 6.60 (br, 4H, H_t), 7.32 (d, 2H, H_b, ^3J = 7.7 Hz), 7.39-7.48 (m, 12H, H_{o-p}), 7.64 (t, 1H, H_a, ^3J = 7.7 Hz), 7.80 (d.d.t., 8H, H_n, ^3J = 12.3 Hz, ^4J = 5.8 Hz, $^3J_{P-H}$ = 1.5 Hz), 8.21 (d, 2H, H_u, ^3J = 5.3 Hz)

^{13}C-NMR (CD_2Cl_2, 125 MHz) (assignments according to HSQC and HMBC 2D ^{1}H-^{13}C NMR experiments): δ (ppm) = 28.8 (C_l, $^1J_{P-C}$ = 18.5 Hz), 67.4 (C_k), 70.68, 70.72, 70.85, 70.98, 71.02, 71.13, 74.4 (C_d), 109.7 (H_r), 120.6 (C_b), 125.9 (H_t), 128.7 (C_n, $^2J_{P-C}$ = 5.2 Hz), 131.1 (C_p), 131.5 (C_m, $^1J_{P-C}$ = 28.6 Hz), 134.0 (C_o, $^3J_{P-C}$ = 5.9 Hz), 136.9 (H_s), 137.6 (C_a), 148.7 (H_u), 158.4 (C_c)

^{31}P-NMR (CD_2Cl_2, 162 MHz): δ (ppm) = 6.02 (J_{P-Pt} = 1249 Hz)

UV-Vis (CH_2Cl_2) λ_{max} (nm) (ε, mol^{-1}·L·cm^{-1}): 230 (1.7·10^4), 265 (1.3·10^4), 291 (1.1·10^4), 338 (1.2·10^4)

MS (ESI): m/z calcd for $C_{61}H_{67}N_3O_8P_2PtH^+$: 1227.413 g·mol^{-1} ; found: 1227.450 g·mol^{-1}

Compound 1-Ag$^+$: To a solution of compound **1** (4.0 mg, 3.26 μmol, 1 eq.) in dry degassed CH_2Cl_2 (2 mL), a solution of $AgSbF_6$ (1.1 mg, 3.26 μmol, 1 eq.) in dry CH_3CN (1 mL) was added. The reaction mixture was stirred at RT in the dark for 2 h. After removal of the solvent, the desired product was obtained quantitatively as a yellow solid.

^{1}H-NMR (CD_2Cl_2, 500 MHz): δ (ppm) = 3.24 (br, 4H, H_l), 3.50-3.55 (m, 8H, H_{i-j}), 3.57 (m, 4H, H_h), 3.62 (m, 4H, H_g), 3.71 (br, 4H, H_f), 3.76-3.83 (br, 8H, H_{e-k}), 4.73 (s, 4H, H_d), 6.92 (br, 4H, H_t), 7.44 (d, 2H, H_b, ^3J = 7.5 Hz), 7.43-7.53 (m, 12H, H_{o-p}), 7.80 (d.d.t., 8H, H_n, ^3J = 12.5 Hz, ^4J = 5.8 Hz, $^3J_{P-H}$ = 1.3 Hz), 7.96 (t, 1H, H_a, ^3J = 7.8 Hz), 8.35 (br, 2H, H_u)

^{13}C-NMR (CD_2Cl_2, 125 MHz) (assignments according to HSQC and HMBC 2D ^{1}H-^{13}C-NMR experiments): δ (ppm) = 28.2 (C_l), 67.1 (C_k), 70.16, 70.66, 70.75, 71.06, 71.14, 71.35, 72.4 (C_d), 123.6 (C_b), 128.4 (C_o), 130.9 (C_p), 133.4 (C_n), 140.5(C_a), 150.3 (C_u), 157.4 (C_c)

^{31}P-NMR (CD_2Cl_2, 162 MHz): δ (ppm) = 2.73 (J_{P-Pt} = 1245 Hz)

UV-Vis (CH_2Cl_2) λ_{max} (nm) (ε, mol^{-1}·L·cm^{-1}): 230 (1.6·10^4), 270 (8.8·10^3), 300 (7.2·10^3), 349 (1.0·10^4)

MS (ESI): m/z calcd for $C_{61}H_{67}N_3O_8P_2PtAg^+$: 1334.31 g·mol^{-1}; found: 1334.32 g·mol^{-1}

General procedure for the titration experiment: To a solution of compound **1** (1 eq.) in dry and degassed CH_2Cl_2 (2 mL), a solution of $AgSbF_6$ (0.25 eq.) in dry CH_3CN (1 mL) was added. The reaction mixture was stirred at RT in the dark for 2 h. After removal of the solvent, the desired product was obtained quantitatively as a yellow solid. The same experimental procedure was repeated with 0.5, 0.75, 1, 2, and 3 eq. of $AgSbF_6$.

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