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Supporting Information

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Supporting Information

A Novel 'Ion Pair' Template for Rotaxane Formation and its Exploitation in an Orthogonal Interaction Anion Switchable Molecular Shuttle

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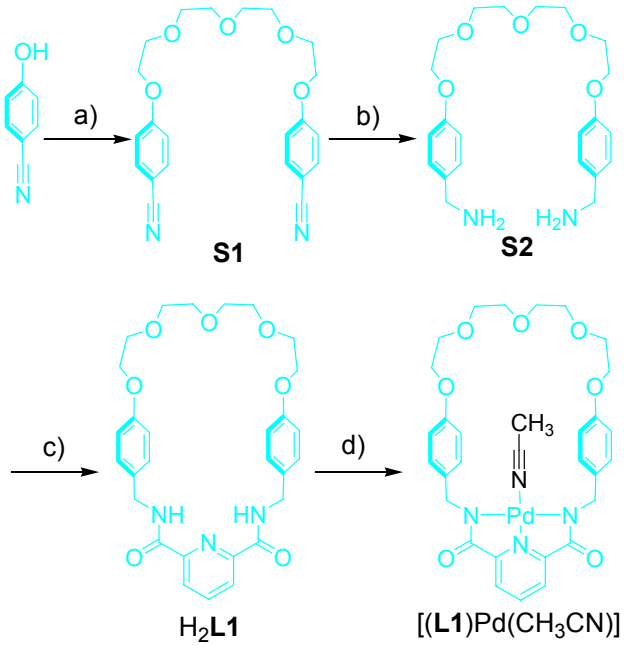
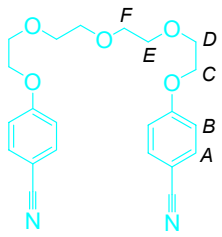
1. General Experimental

Unless stated otherwise, all reagents and solvents were purchased from Aldrich Chemicals and used without further purification. Tetrahydrofuran, dichloromethane, chloroform, acetonitrile and *N*,*N*-dimethylformamide were dried using a solvent purification system manufactured by Innovative Technology, Newburyport, MA, USA. 4-[*tris*-(4-*tert*-butylphenyl)methyl]phenol[1] and 1-(3-azidopropoxy)-4-(*tris*-(4-tert-butylphenyl)methyl)benzene[2] **3** were prepared according to literature procedures. Unless stated otherwise, all reactions were carried out under an atmosphere of nitrogen. Column chromatography was carried out using Silica 60A (particle size 35-70 μm, Fisher, UK) as the stationary phase, and TLC was performed on precoated silica gel plates (0.25 mm thick, 60 F_{254}, Merck, Germany) and observed under UV light. All ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV 400 instrument, at a constant temperature of 298 K. Chemical shifts are reported in parts per million from low to high field. Coupling constants (*J*) are reported in hertz (Hz). Standard abbreviations indicating multiplicity are used as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Other abbreviations used in the Supporting Information include RT = room temperature, DIAD = diisopropylazodicarboxylate, DIPEA = diisopropylethylamine, TBTA = *tris*-(benzyltriazolylmethyl)amine. Melting points (m.p.) were determined using a Sanyo Gallenkamp apparatus. Mass spectrometry was carried out by the services at the University of Edinburgh and at the EPSRC National Mass Spectrometry Service Centre, Swansea.

2. Synthesis of [(**L1**)Pd(CH_3CN)]



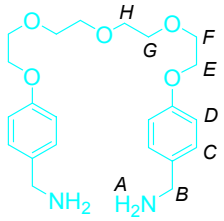
Scheme 1. Reagents and conditions: a) tetra-(ethyleneglycol)di-*p*-toluene sulfonate, K_2CO_3, butanone, reflux, 5 days, 88%; b) $LiAlH_4$, THF, 0→60 °C, 3 h, 78%; c) pyridine-2,6-dicarbonyl chloride, CH_2Cl_2, NEt_3, 0 °C →RT, 3 days, 61%; d) $Pd(OAc)_2$, CH_3CN, RT, 5 h, 71%.



S1

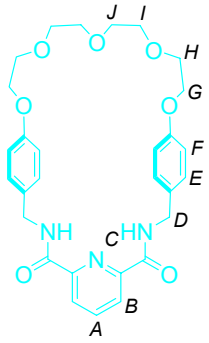
To a solution of 4-hydroxybenzonitrile (4.48 g, 37.6 mmol) and tetra-(ethyleneglycol)di-*p*-toluene sulfonate (9.28 g, 18.5 mmol) in butanone (500 mL), was added K_2CO_3 (14.1 g, 102 mmol). The mixture was heated to reflux for 5 days. After cooling to RT, the K_2CO_3 was separated by filtration. The solvent was then removed under reduced pressure and the resulting crude residue purified by column chromatography (CH_2Cl_2:EtOAc 90:10) to give **S1** as a colorless solid (6.47 g,

88%). m.p. 50-52 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.65-3.67 (m, 4H, H_F), 3.69-3.72 (m, 4H, H_E), 3.84-3.86 (m, 4H, H_D), 4.14-4.16 (m, 4H, H_C), 6.95 (d, J = 8.9, 4H, H_B), 7.55 (d, J = 8.9, 4H, H_A); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 67.7, 69.4, 70.6, 70.9, 104.1, 115.3; 119.2, 134.0, 162.1; HREI-MS: m/z = 419.15902 $[M+Na]^+$ (calcd. for $C_{22}H_{24}O_5N_2Na$, 419.15774).



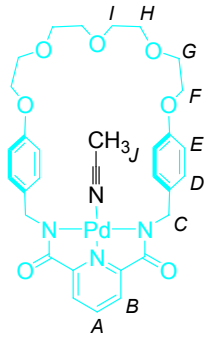
S2

To a solution of 1M $LiAlH_4$ in THF (100 mL, 100 mmol) at 0°C was added a solution of **S1** (6.36 g, 16.0 mmol) in THF (100 mL) dropwise. Following the precipitation of a yellow solid, the mixture was heated at reflux for 3 h. The flask was then cooled to 0 °C and water (3.8 mL) was added, followed by 15% aqueous NaOH solution (3.8 mL) and finally water (11.4 mL). The aluminium salts were removed by filtration and the filtrate concentrated under reduced pressure to give a colorless solid (4.98 g, 78%) which was used without further purification. m.p. 130-133 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 1.61 (br, 4H, H_A), 3.67-3.69 (m, 4H, H_H), 3.71-3.74 (m, 4H, H_G), 3.78 (s, 4H, H_B), 3.83-3.85 (m, 4H, H_F), 4.09-4.11 (m, 4H, H_E), 6.87 (d, J = 8.6, 4H, H_D), 7.20 (d, J = 8.6, 4H, H_C); ^{13}C NMR (100 MHz, DMF-d_7): δ= 45.4, 67.5, 69.5, 70.4, 70.5, 114.6, 128.4, 162.0, 176.2; HRESI-MS: m/z = 405.2383 $[MH]^+$ (calcd. for $C_{22}H_{33}O_5N_2$, 405.2384).



H_2**L1**

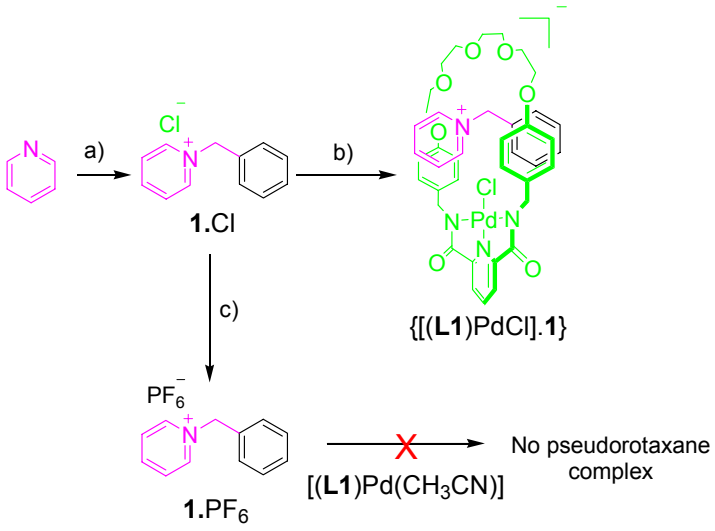
To a solution of **S2** (4.39 g, 10.9 mmol) and NEt_3 (3 mL) in CH_2Cl_2 (2 L) at 0 °C was added a solution of pyridine-2,6-dicarbonyl chloride (2.07 g, 10.9 mmol,) in CH_2Cl_2 (20 mL) dropwise over a period of 4 h. The solution was then stirred at RT for 3 days. After this time the solvent was removed under reduced pressure and the crude material purified by flash chromatography (CH_2Cl_2:MeOH 95:5) to give H_2**L1** as a colorless solid (3.44 g, 61%). m.p. 192-195 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.67-3.73 (m, 8H, H_{I+J}), 3.89-3.91 (m, 4H, H_H), 4.08-4.10 (m, 4H, H_G), 4.57 (d, J = 5.6, 4H, H_D), 6.77 (d, J = 8.6, 4H, H_F), 7.12 (d, J = 8.6, 4H, H_E), 7.89 (t, J = 5.6, 2H, H_C), 8.04 (t, J = 7.8, 1H, H_A), 8.36 (d, J = 7.8, 2H, H_B); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 42.9, 67.5, 69.6, 70.6, 70.7, 114.5, 125.1, 128.8, 130.0, 139.0, 148.7, 158.0, 163.3; HRESI-MS: *m/z* = 536.2383 $[MH]^+$ (calcd. for $C_{29}H_{34}O_7N_3$, 536.2391).



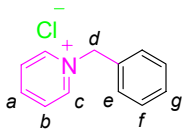
[(**L1**)Pd(CH_3CN)]

To a solution of H_2**L1** (1.02 g, 1.91 mmol) in CH_3CN (100 mL) was added $Pd(OAc)_2$ (472 mg, 2.10 mmol). The reaction was stirred for 5 h, after which time a yellow precipitate was collected by filtration and recrystallized from CH_3CN to give a yellow crystalline solid (927 mg, 71%). m.p. 238-240 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$:CD_3CN 98:2): δ = 1.98 (s, 3H, H_J), 3.64-3.65 (m, 4H, H_I), 3.67-3.69 (m, 4H, H_H), 3.80-3.82 (m, 4H, H_G), 4.02-4.04 (m, 4H, H_F), 4.51 (s, 4H, H_C), 6.76 (d, J = 8.6, 4H, H_E), 7.16 (d, J = 8.6, 4H, H_D), 7.77 (d, J = 7.8, 2H, H_B), 8.07 (t, J = 7.8, 1H, H_A); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.2, 47.3, 66.0, 68.3, 69.0, 69.2, 112.5, 115.1, 123.5, 126.6, 132.4, 139.5, 151.9, 155.8, 169.0; LRESI-MS: m/z = 639 $[M\text{-}CH_3CN]^+$.

3. Synthesis of **1**.Cl, **1**.PF_6 and {[(**L1**)PdCl].**1**}

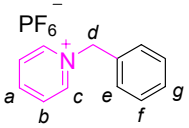


Scheme 2. Synthesis of the pseudorotaxane {[(**L1**)PdCl].**1**}. Reagents and conditions: a) Benzyl chloride, toluene, reflux, 5 days, 80%; a) [(**L1**)Pd(CH_3CN)], $CDCl_3$, RT, 2 h, quant; c) $AgPF_6$, acetone, RT, 18 h, quant.



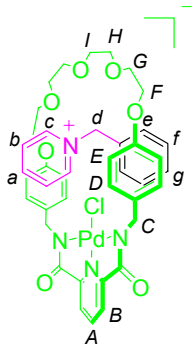
1.Cl

A solution of pyridine (700 µL, 8.68 mmol) and benzyl chloride (1.10 g, 8.69 mmol) in toluene (20 mL) was heated at reflux for 5 days. The resulting precipitate was collected and washed with hexane to give **1**.Cl as a colorless, hydroscopic solid (1.45 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.18 (s, 2H, H_d), 7.22-7.30 (m, 3H, H_{f+g}), 7.62-7.64 (m, 2H, H_e), 7.96-7.98 (m, 2H, H_b), 8.42 (t, J = 5.6, 1H, H_a), 9.69 (d, J = 5.6, 2H, H_c); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 63.1, 127.8, 128.8, 128.9, 129.2, 132.9, 144.6, 144.7; HRESI-MS: m/z = 170.0964 $[M\text{-}Cl]^+$ (calcd. for $C_{12}H_{12}N_1$, 170.0964).



1.PF_6

To a solution of **1**.Cl (88 mg, 0.43 mmol) in acetone (5 mL) was added $AgPF_6$ (108 mg, 0.43 mmol). The solution was stirred in the absence of light for 18 h, after which time the white precipitate was removed by filtration and the filtrate concentrated under vacuum to give **1**.PF_6 as a colorless solid (130 mg, quant.). m.p. 135-137 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.66 (s, 2H, H_d), 7.34 (br, 5H, H_{e+f+g}), 7.96 (br, 2H, H_b), 8.41 (br, 1H, H_a), 8.70 (br, 2H, H_c); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 63.8, 115.4, 127.4, 128.0, 128.5, 129.0, 142.9, 144.7; HRESI-MS: m/z = 170.0965 $[M\text{-}PF_6]^+$ (calcd. for $C_{12}H_{12}N_1$, 170.0964).



{[(**L1**)PdCl].**1**}

1.Cl (23 mg, 0.11 mmol) and [(**L1**)Pd(CH_3CN)] (76 mg, 0.11 mmol) were dissolved in $CDCl_3$ (2 mL) and stirred for 1 h. The solvent was then removed under reduced pressure to give {[(**L1**)PdCl].**1**} as a bright yellow solid (99 mg, quant.), which could be recrystallized by slow evaporation of a saturated CH_2Cl_2/EtOAc solution to give single crystals suitable for investigation by X-ray crystallography. m.p. 142-145 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.25-3.41 (br, 4H, H_I), 3.60-3.71 (m, 12H, $H_{F,G,H}$), 3.90 (d, J = 13.5, 2H, H_C), 5.16 (t, J = 13.5, 2H, $H_{C'}$), 5.32 (s, 2H, H_d), 5.95 (d, J = 8.5, 4H, H_E), 7.08 (d, J = 8.5, 4H, H_D), 7.41 (br, 5H, $H_{e,f,g}$), 7.59-7.63 (m, 2H, H_b), 7.77-7.84 (m, 3H, H_{a+B}), 7.97 (t, J = 7.9, 1H, H_A), 8.45, (d, J = 5.7, 2H, H_c); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 48.1, 64.5, 66.6, 69.8, 70.4, 70.9, 112.4, 124.2, 127.4, 129.4, 129.5, 130.0, 130.2, 132.0, 135.7, 139.2, 143.4, 143.7, 153.2, 155.5, 170.8.

4. ^{1}H NMR analysis of {[(**L1**)PdCl].**1**}

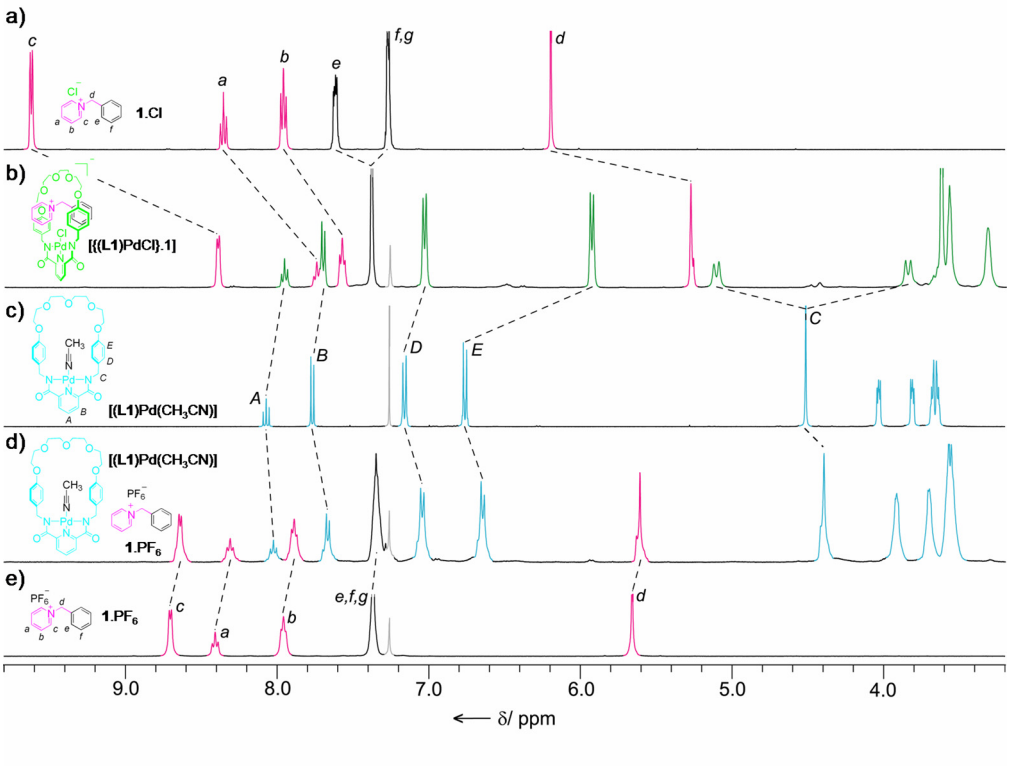


Figure S1. Partial ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectra of: a) **1**.Cl; b) {[(**L1**)PdCl].**1**}; c) [(**L1**)Pd(CH_3CN)]; d) 1:1 mixture of [(**L1**)Pd(CH_3CN)] and **1**.PF_6; e) **1**.PF_6.

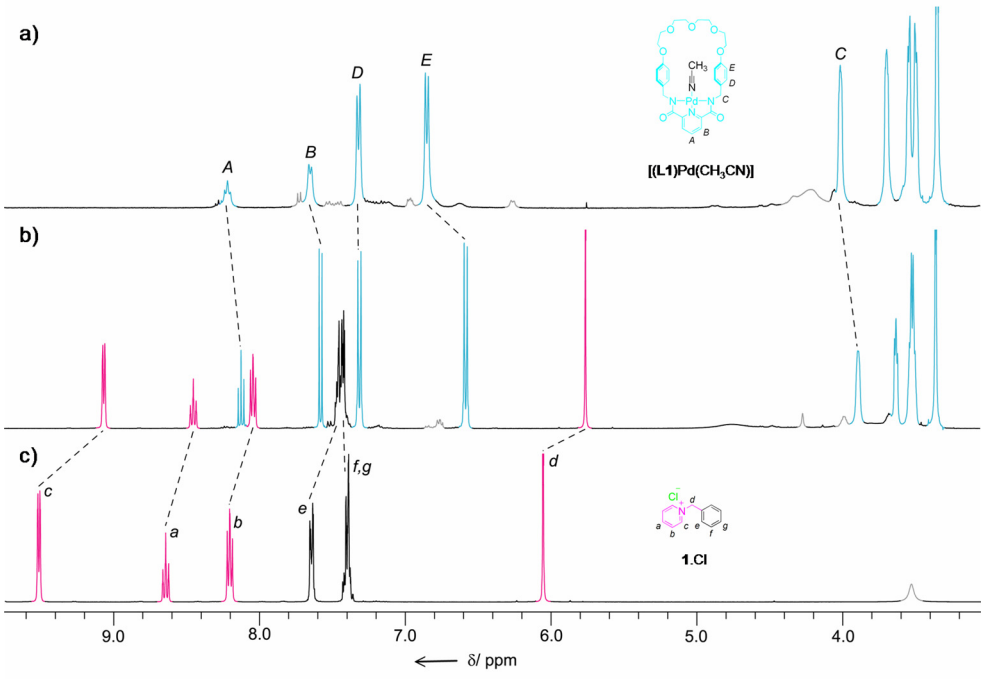
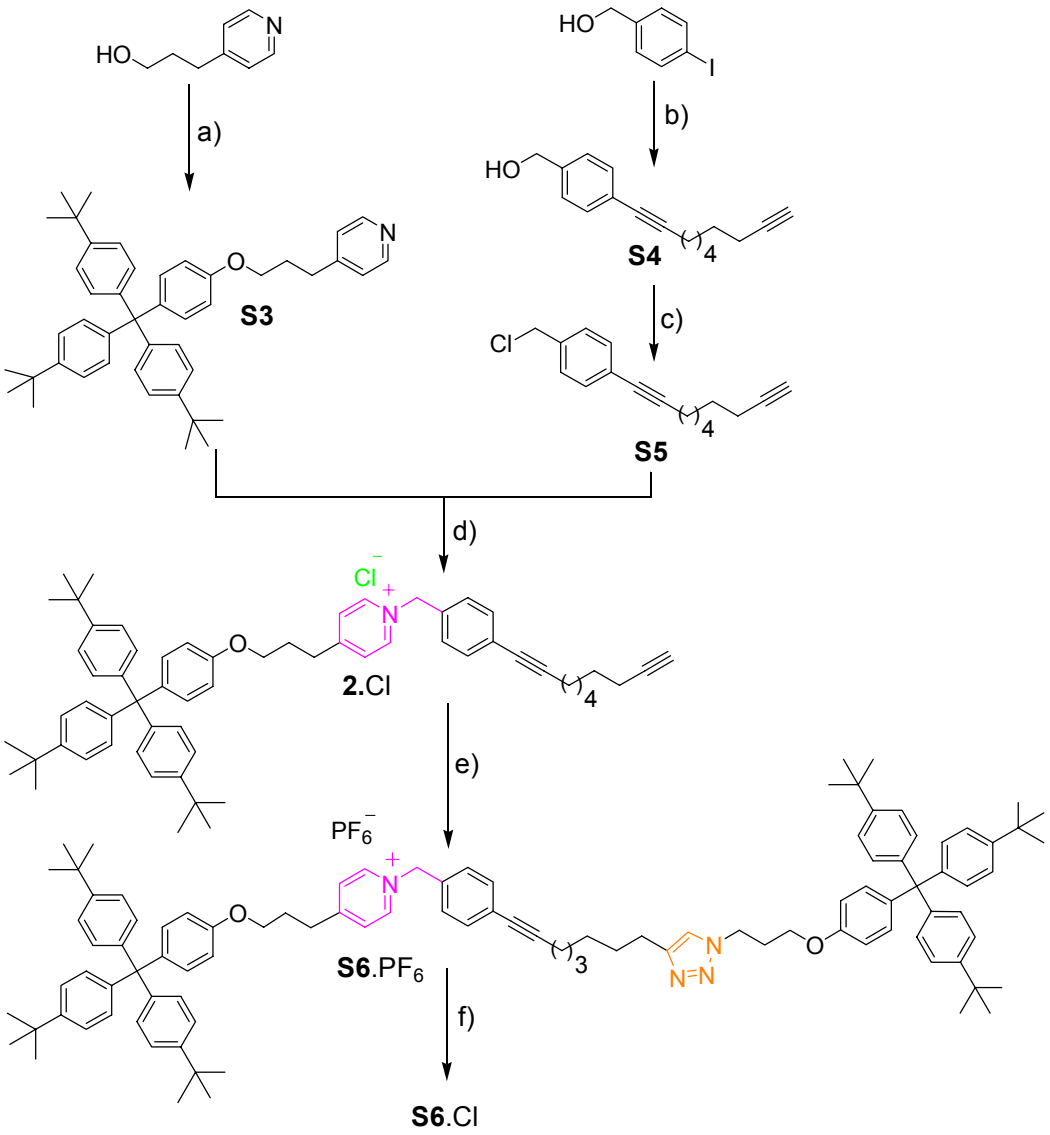
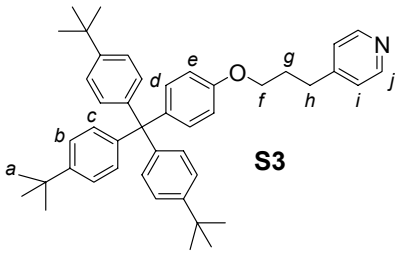


Figure S2. Partial ^{1}H NMR (400 MHz, [D_6]DMSO, 298 K) spectra of: a) [(**L1**)Pd(CH_3CN)]; b) [(**L1**)PdCl].**1**; c) **1**.Cl.

5. Synthesis of **2**.Cl and the chloride and PF_6 salts of the thread (**S6**$^+$)

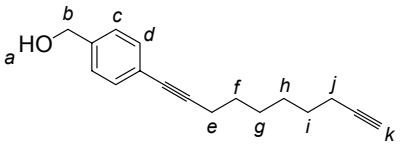


Scheme 3. Synthesis of thread precursor **2**.Cl and thread **S6**$^+$. Reagents and conditions: a) 4-[tris-(4-*tert*-butylphenyl)methyl]phenol, DIAD, PPh_3, THF, 0 °C→RT, 18 h, 93%; b) 1,9-decadiyne, CuI, $Pd(PPh_3)_2Cl_2$, NEt_3, THF, RT, 18 h, 86%; c) $SOCl_2$, CH_2Cl_2, NEt_3, 0 °C → reflux, 2 h, 84%; d) CH_3CN, reflux, 7 days, 48%; e) 1-(3-azidopropoxy)-4-(tris-(4-tert-butyl-phenyl)methyl)benzene **3**, DIPEA, $Cu(CH_3CN)_4PF_6$, CH_2Cl_2, MeOH, RT, 18 h, 32%; f) NH_4Cl, 100%.



S3

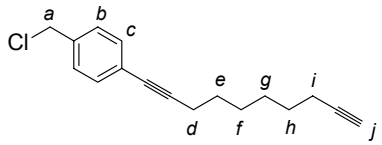
To a solution of 4-[tris-(4-*tert*-butylphenyl)methyl]phenol (1.00 g, 1.98 mmol), 4-pyridinepropan-1-ol (272 mg, 1.98 mmol) and PPh_3 (2.06 g, 7.86 mmol) in THF (100 mL) at 0 ˚C was added DIAD (0.80 mL, 3.96 mmol) dropwise. Once warmed to RT, the reaction was stirred for 18 h. The volatile compounds were then removed under reduced pressure and the resulting material purified by flash chromatography (hexane:EtOAc 2:1) to give **S3** as a colorless solid (1.18 g, 93%). m.p. 235-237 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.30 (s, 27H, H_a), 2.07-2.13 (m, 2H, H_g), 2.81 (t, J = 7.4, 2H, H_h) 3.94 (t, J = 6.1, 2H, H_f), 6.74 (d, J = 8.9, 2H, H_e), 7.08 (m, 8H, H_{c+d}), 7.15 (d, J = 5.6, 2H, H_i), 7.23 (d, J = 8.6, 6H, H_b), 8.50 (d, J = 5.6, 2H, H_j); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.0, 29.8, 31.4, 31.6, 34.3, 66.4, 112.9, 123.9, 124.0, 130.7, 132.3, 139.7, 144.1, 148.3, 149.8, 150.6, 156.6; HRESI-MS: *m/z* = 624.4196 $[MH]^+$ (calcd. for $C_{45}H_{54}O_1N_1$, 624.4200).



S4

To a solution of 4-iodobenzyl alcohol (4.30 g, 18.3 mmol) and 1,9-decadiyne (9.22 g, 68.7 mmol) in THF (160 mL) and NEt_3 (40 ml) was added CuI (410 mg, 2.15 mmol) and $Pd(PPh_3)_2Cl_2$ (618 mg, 0.88 mmol). The solution was subsequently stirred for 18 h after which time the volatile compounds were removed under reduced pressure.

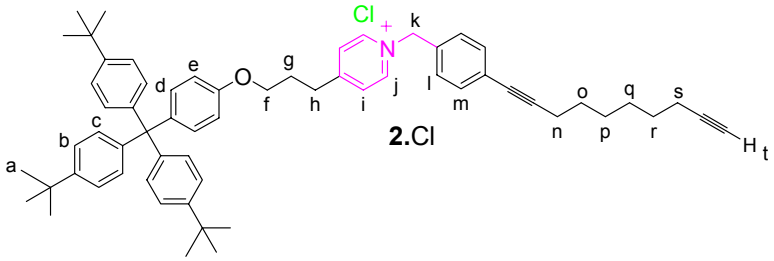
The resulting residue was dissolved in CH_2Cl_2 (100 mL) and washed with saturated aqueous NH_4Cl (3 x 50 mL). The aqueous phase was extracted with CH_2Cl_2 (3 x 50 mL) and the combined organic extracts dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the resulting residue purified by flash chromatography (hexane:EtOAc 2:1), providing **S4** as a pale yellow oil (3.81 g, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.45-1.63 (m, 8H, $H_{f+g+h+i}$), 1.88 (br, 1H, H_a), 1.95 (t, J = 2.6, 1H, H_k), 2.20 (td, J = 2.6, 7.0, 2H, H_j), 2.41 (t, J = 7.1, 2H, H_e), 4.66 (s, 2H, H_b), 7.27 (d, J = 8.0, 2H, H_d), 7.38 (d, J = 8.0, 2H, H_c); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.3, 19.4, 28.2, 28.3, 28.4, 28.6, 65.0, 68.2, 80.5, 84.7, 90.4, 123.3, 126.8, 131.7, 140.2; HRCI-MS: m/z = 258.1855 $[M+NH_4]^+$ (calc. for $C_{17}H_{24}O_1N_1$, 258.1852).



S5

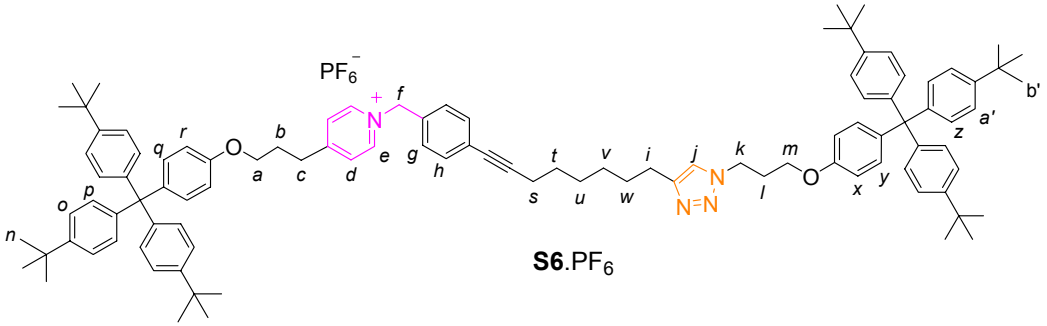
To a solution of **S4** (3.60 g, 15.0 mmol) in CH_2Cl_2 (100 mL) and NEt_3 (20 mL) at 0˚C was added $SOCl_2$ (5.5 mL, 74.9 mmol) dropwise. The solution was allowed to gradually return to RT before being heated at reflux for 2 h. After cooling back to RT, the reaction was washed with water (3 x 100mL) and the aqueous phase extracted with CH_2Cl_2 (3 x 50 mL). The combined organic extracts were dried over anhydrous $MgSO_4$ and the solvent removed under reduced pressure. The resulting residue was passed through a plug of silica (hexane) to provide **S5** as a dark red oil (3.25 g, 84%) which was used directly without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.42-1.51 (m, 4H, H_{f+g}), 1.53-1.65 (m, 4H, H_{e+h}), 1.95 (t, J = 2.6, 1H, H_j), 2.24 (td, J = 2.6, 6.9, 2H, H_i), 2.41 (t, J = 7.08, 2H, H_d), 4.56 (s, 2H, H_a), 7.30 (d, J = 8.4, 2H,

H_c), 7.38 (d, J = 8.4, 2H, H_b); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.4, 19.4, 28.2, 28.3, 28.4, 28.5, 46.0, 68.2, 80.2, 84.6, 91.2, 124.2, 128.5, 131.8, 136.6.



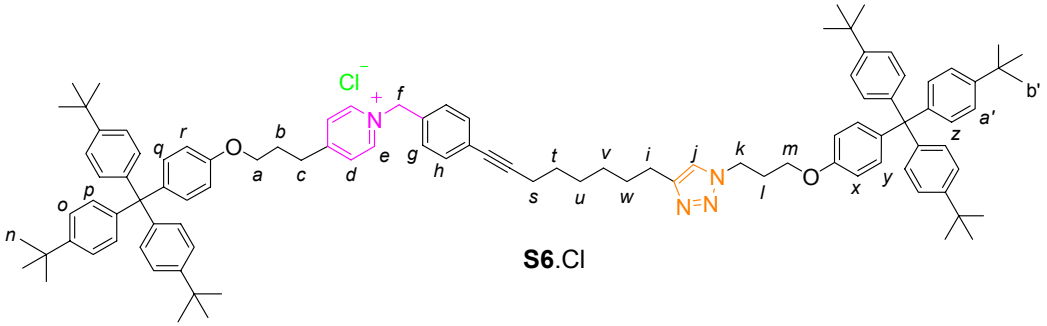
2.Cl

A solution of **S3** (2.82 g, 4.40 mmol) and **S5 (**1.16 g, 4.47 mmol) in acetonitrile (150 mL) was heated to reflux for 7 days. After cooling the solvent was removed under reduced pressure and the resulting material purified by flash chromatography (CH_2Cl_2:MeOH 9:1) to give **2.**Cl as a pale yellow solid (1.89 g, 48%). m.p. 172-175 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.29 (s, 27H, H_a), 1.41-1.44 (m, 4H, H_{p+q}), 1.50-1.60 (m, 4H, H_{o+r}), 1.92 (t, J = 2.6 Hz, 1H, H_t), 2.07-2.14 (m, 2H, H_g), 2.18 (td, J = 2.6, 7.0, 2H, H_s), 2.36 (t, J = 7.09, 2H, H_n), 3.03 (t, J = 7.87, 2H, H_h), 3.95 (t, J = 5.5, 2H, H_f), 6.30 (s, 2H, H_k), 6.66 (d, J = 8.9, 2H, H_e), 7.06 (d, J = 8.6, 6H, H_c), 7.07 (d, J = 8.9, 2H, H_d), 7.22 (d, J = 8.6, 6H, H_b), 7.35 (d, J = 8.2, 2H, H_m), 7.58 (d, J = 8.2, 2H, H_l), 7.75 (d, J = 6.6, 2H, H_i), 9.48 (d, J = 6.6, 2H, H_j); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.3, 19.3, 28.1, 28.2, 28.3, 28.4, 29.0, 31.2, 32.6, 34.3, 62.7, 63.0, 65.9, 68.3, 79.8, 84.5, 92.2, 112.78, 124.3, 125.7, 127.9, 129.6, 131.0, 132.3, 132.5, 132.7, 140.0, 144.0, 144.5, 148.3, 156.1, 162.2; HRFAB-MS (3-NOBA matrix): m/z = 846.56149 $[M\text{-}Cl]^+$ (calc. for $C_{62}H_{72}NO$, 846.56139).



S6.PF_6

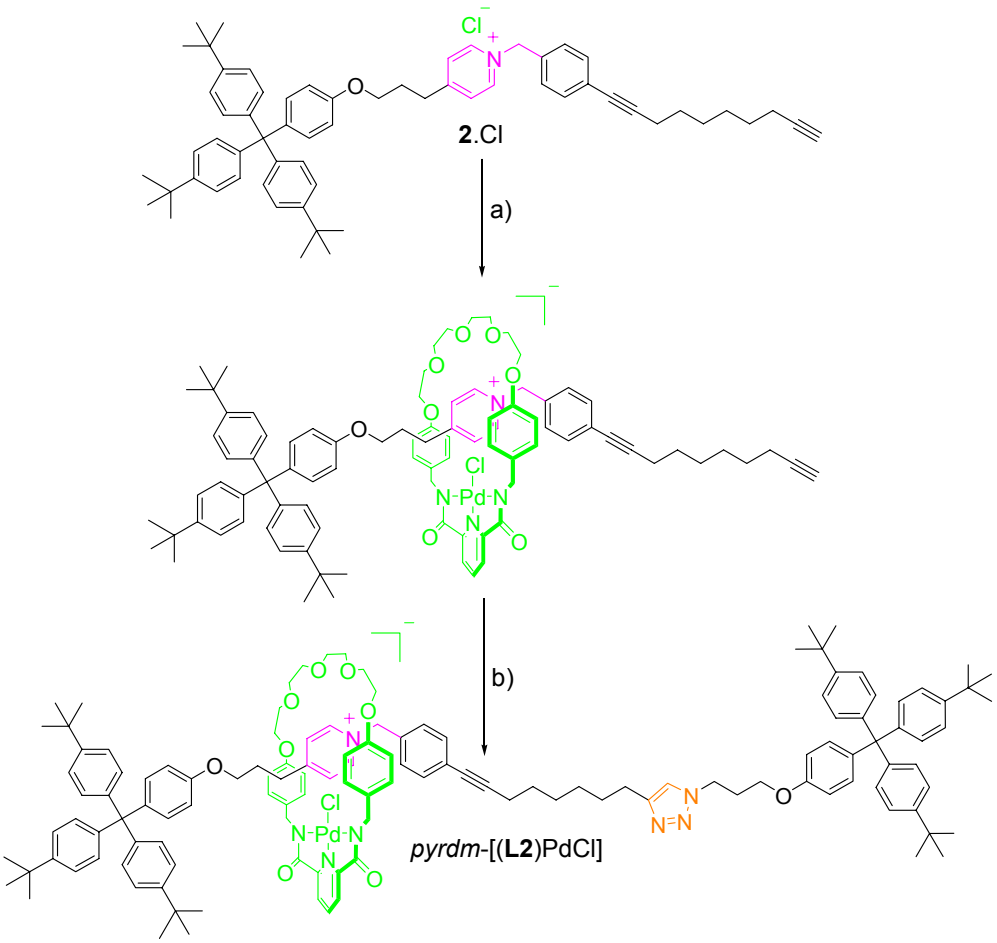
To a solution of **2.**Cl (155 mg, 0.17 mmol) and **3** (108 mg, 0.18 mmol) in CH_2Cl_2 (7 mL) and MeOH (1 mL) was added $Cu(CH_3CN)_4PF_6$ (67 mg, 0.18 mmol) and DIPEA (150 µL, 0.86 mmol). The solution was stirred for 18 h and after this time the volatile compounds were removed under reduced pressure. The resulting residue was purified by column chromatography (CH_2Cl_2:MeOH 95:5) to give **S6**.PF_6 as an off-white solid (88 mg, 32%). m.p. 190-193 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.29 (s, 54H, $H_{n+b'}$), 1.36-1.49 (m, 4H, H_{u+v}), 1.54-1.61 (m, 2H, H_w), 1.64-1.71 (m, 2H, H_t), 2.09-2.16 (m, 2H, H_b), 2.32-2.37 (m, 4H, H_{s+l}), 2.70 (t, J = 7.7, 2H, H_i), 3.06 (t, J = 7.6, 2H, H_c), 3.92 (t, J = 5.7, 2H, H_m), 3.96 (t, J = 5.7, 2H, H_a), 4.52 (t, J = 6.9, 2H, H_k), 5.73 (s, 2H, H_f), 6.67 (d, J = 8.9, 2H, H_r), 6.73 (d, J = 8.9, 2H, H_x), 7.05-7.10 (m, 16H, $H_{p+q+y+z}$), 7.21-7.23 (m, 13H, $H_{o+a'+j}$), 7.32-7.41 (m, 4H, H_{g+h}), 7.77 (d, J = 5.8, 2H, H_d), 8.69 (d, J = 5.8, 2H, H_e); HRFAB-MS (3-NOBA matrix): *m/z* = 1434.95669 $[M\text{-}PF_6]^+$ (calc. for $C_{101}H_{121}{}^{13}CN_4O_2$, 1434.95231).



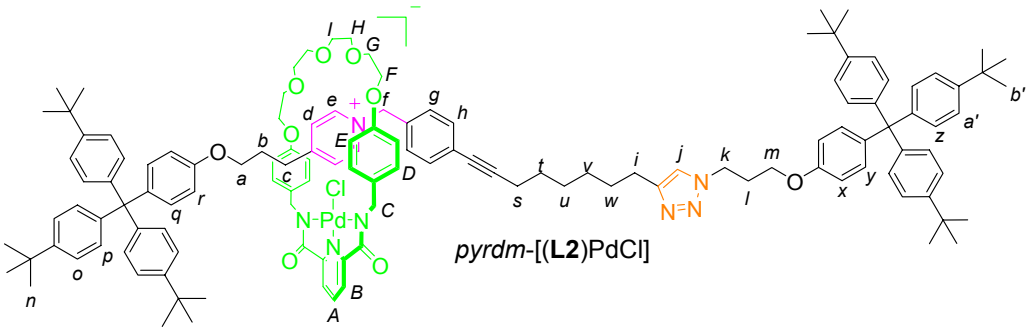
S6.Cl

S6.PF_6 (56 mg, 0.035 mmol) was dissolved in $CHCl_3$ (10 mL) and washed repeatedly with saturated aqueous NH_4Cl (10 x 50 mL). The organic phase was then washed with water (1 x 50 mL) and the solvent removed under reduced pressure to give **S6**.Cl as a colorless solid (51 mg, quant.). m.p. 180-182 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.29 (s, 54H, $H_{n+b'}$), 1.34-1.42 (m, 4H, H_{u+v}), 1.54-1.61 (m, 2H, H_w), 1.63-1.71 (m, 2H, H_t), 2.12-2.19 (br, 2H, H_b), 2.34-2.37 (m, 4H, H_{s+l}), 2.70 (t, J = 7.6, 2H, H_i), 3.06-3.09 (m, 2H, H_c), 3.93 (t, J = 5.6, 2H, H_m), 3.95-4.00 (m, 2H, H_a), 4.53 (t, J = 6.7, 2H, H_k), 6.19 (br, 2H, H_f), 6.67 (d, J = 8.7, 2H, H_r), 6.73 (d, J = 8.9, 2H, H_x), 7.06-7.10 (m, 16H, $H_{p+q+y+z}$), 7.21-7.24 (m, 13H, $H_{o+a'+f}$), 7.35-7.39 (m, 2H, H_h), 7.47-7.53 (m, 2H, H_g), 7.78 (br, 2H, H_d), 9.35 (br, 2H, H_e). HRFAB-MS (3-NOBA matrix): m/z = 1434.95886 $[M\text{-}Cl]^+$ (calc. for $C_{101}{}^{13}CH_{121}N_4O_2$, 1434.95231).

6. Synthesis of *pyrdm*-[(L2)PdCl]



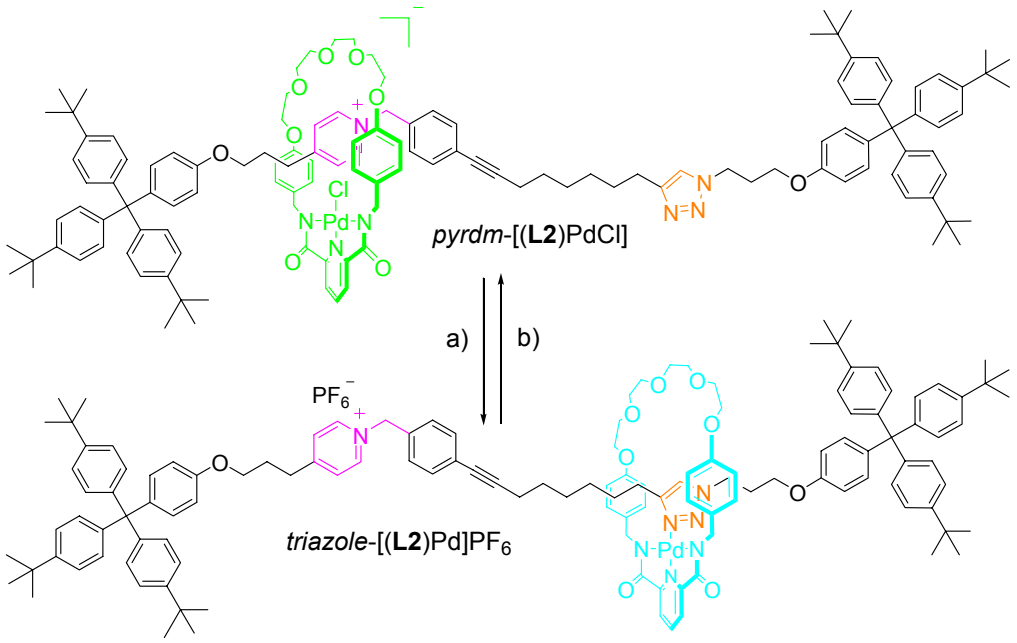
Scheme 4. Synthesis of *pyrdm*-[(**L2**)PdCl]. Reagents and conditions: a) [(**L1**)Pd(CH_3CN)], CH_2Cl_2, RT, 1 h; b) 1-(3-azidopropoxy)-4-(tris-(4-tert-butylphenyl)methyl)benzene **3**, DIPEA, TBTA, $Cu(CH_3CN)_4PF_6$, CH_2Cl_2, CH_3CN, RT, 18 h, 64% (from **2**.Cl).



2.Cl (59 mg, 0.066 mmol) and [(**L1**)Pd(CH_3CN)] (50 mg, 0.073 mmol) were dissolved in a mixture of CH_2Cl_2 (7 mL), and then stirred for 1 h before **3** (43 mg, 0.073 mmol) and DIPEA (11 µL, 0.066 mmol) were added. A solution of TBTA (9 mg, 0.017 mmol) and $Cu(CH_3CN)_4PF_6$ (6 mg, 0.0147 mmol) in CH_3CN (1 mL) was then added and the reaction mixture stirred for a further 18 h. After this time the volatile compounds were removed under reduced pressure and the resulting residue dissolved in CH_2Cl_2 (10 mL). The solution was washed with NH_4Cl (3 x 10 mL) and the aqueous phase re-extracted with CH_2Cl_2 (3 x 5 mL). The combined organic phase was concentrated under reduced pressure and the crude material subjected to flash chromatography on silica gel (0-3% MeOH in CH_2Cl_2) to give *pyrdm*-[(**L2**)PdCl] as a bright yellow solid (89 mg, 64%). m.p. 197-200 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.29 (s, 27H, H_n), 1.30 (s, 27H, $H_{b'}$), 1.37-1.43 (m, 2H, H_u), 1.45-1.51 (m, 2H, H_v), 1.56-1.62 (m, 2H, H_t), 1.67-1.72 (m, 2H, H_w), 1.75 (br, 2H, H_b), 2.32-2.40 (m, 4H, H_{l+s}), 2.59-2.64 (m, 2H, H_c), 2.70 (t, J = 7.7, 2H, H_i), 3.21 (t, J = 9.5, 4H, H_G), 3.35-3.39 (m, 6H, H_{a+F}), 3.52-3.69 (m, 8H, H_{H+I}), 3.86-3.95 (m, 4H, H_{C+m}), 4.52 (t, J = 7.0, 2H, H_k), 5.20 (d, J = 13.4, 2H, $H_{C'}$), 5.29 (s, 2H, H_f), 5.88 (d, J = 8.6, 4H, H_E), 6.60 (d, J = 8.9, 2H, H_r), 6.74 (d, J = 8.9, 2H, H_x), 7.06-7.13 (m, 20H, $H_{p+q+z+y+D}$), 7.21-7.26 (m, 13H, $H_{o+a'+j}$), 7.52-7.56 (m, 4H, H_{g+h}), 7.62 (br, 3H, H_{A+B}), 7.71 (d, J = 6.5, 2H, H_d), 8.22 (d, J = 6.5, 2H, H_e); ^{13}C NMR (100 MHz,

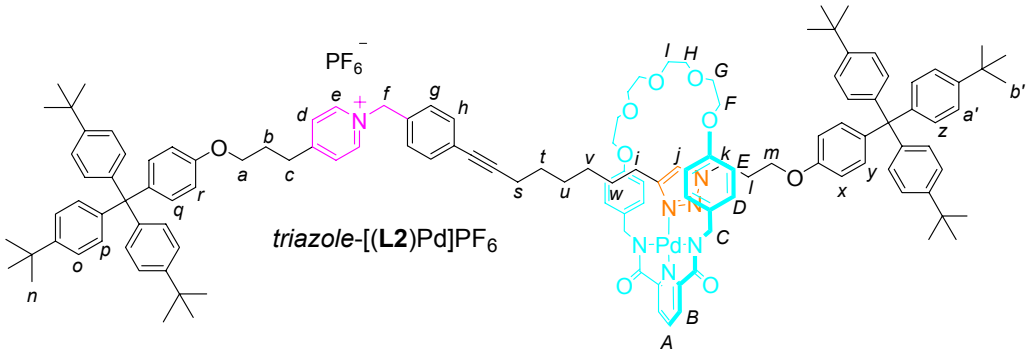
$CDCl_3$): δ= 19.4, 25.6, 28.3, 28.6, 28.7, 29.4, 30.1, 31.3, 32.4, 33.0, 34.2, 34.3, 46.9, 48.3, 62.9, 63.4, 63.9, 65.8, 66.3, 70.0, 70.3, 71.0, 79.6, 92.7, 111.9, 112.4, 112.8, 113.0, 113.3, 121.1, 124.0, 124.1, 124.8, 126.2, 126.8, 127.4, 128.5, 128.9, 129.1, 129.8, 130.1, 131.0, 132.1, 132.3, 132.4, 136.2, 139.2, 140.0, 140.1, 143.1, 144.0, 144.1, 148.3, 153.1, 155.4, 156.0, 156.2, 160.0, 170.7; HRFAB-MS (3-NOBA matrix): *m/z* = 2073.06789 $[M]^+$ (calc. for $C_{130}{}^{13}CH_{152}N_7O_9{}^{105}Pd$, 2073.07359).

7. Chloride-responsive co-conformational switching experiments.



Scheme 5. Reversible switching of the molecular shuttle $[(\mathbf{L2})Pd]^+$. Reagents and conditions: a) $AgPF_6$, Acetone, RT, 18 h, quant.; b) NBu_4Cl, $CDCl_3$, RT, 10 min, quant.

a) Conversion of *pyrdm*-[(**L2**)PdCl] to *triazole*-[(**L2**)Pd]PF_6.



To a solution of *pyrdm*-[(**L2**)PdCl] (44 mg, 0.021 mmol) in acetone (5 mL) was added $AgPF_6$ (6 mg, 0.023 mmol). The solution was stirred in the absence of light for 18 h after which time a white precipitate was removed by filtration, and the filtrate concentrated under reduced pressure to give *triazole*-[(**L2**)Pd]PF_6 as a bright yellow solid (45 mg, quant). m.p. 140-143 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.73 (br, 2H, H_i), 1.12-1.31 (m, 60H, $H_{a+b'+u+v+w}$), 1.51-1.57 (m, 2H, H_t), 2.03-2.10 (m, 2H, H_b), 2.45 (t, J = 6.5, 2H, H_s), 2.52 (m, 2H, H_l), 2.97-3.01 (m, 2H, H_c), 3.10 (d, J = 14.4, 2H, H_C), 3.50-3.77 (m, 12H, H_{G+H+I}), 3.90-3.93 (m, 6H, H_{F+a}), 4.14 (t, J = 5.5, 2H, H_m), 4.63 (t, J = 7.1, 2H, H_k), 5.21 (d, J = 14.4, 2H, $H_{C'}$), 5.66 (s, 2H, H_f), 6.35-6.45 (m, 8H, H_{D+E}), 6.66 (d, J = 8.9, 2H, H_r), 6.84 (d, J = 8.9, 2H, H_x), 6.89 (s, 1H, H_j), 7.04-7.23 (m, 28H, $H_{o+p+q+y+z+a'}$), 7.27-7.41 (m, 4H, H_{g+h}), 7.70 (d, J = 6.6, 2H, H_d), 7.84 (d, J = 7.8, 2H, H_B), 8.14 (t, J = 7.8, 1H, H_A), 8.73 (d, J = 6.6, 2H, H_e).

b) Conversion of *triazole*-[(**L2**)Pd]PF_6 to *pyrdm*-[(**L2**)PdCl].

To a solution of *triazole*-[(**L2**)Pd]PF_6 (35 mg, 0.016 mmol) in $CDCl_3$ (2 mL) was added NBu_4Cl (7 mg, 0.024 mmol) and after 10 min ^{1}H NMR spectroscopy indicated complete conversion to *pyrdm*-[(**L2**)PdCl]. The sample was subsequently washed

with water (3 x 10 mL), the aqueous phase re-extracted with CH_2Cl_2, (3 x 5 mL) and the combined organics extracts dried over anhydrous $MgSO_4$. Removal of the solvent under reduced pressure gave *pyrdm*-[(**L2**)PdCl] as a bright yellow solid (44 mg quant). Physical and spectroscopic data identical to that described for its original synthesis (see above).

8. Crystal Structure Data for {[(**L1**)PdCl].1}

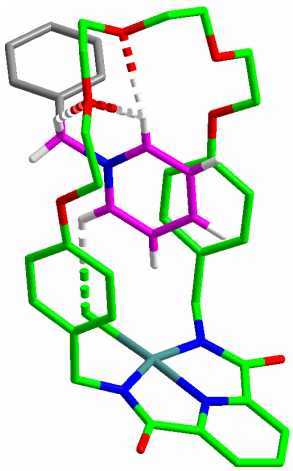


Figure 3. Crystal structure of {[(**L1**)PdCl].**1**}.

CCDC-689628		
Identification code	{[(**L1**)PdCl].**1**}	
Empirical formula	$C_{42}H_{49}Cl_3N_4O_9Pd$	
Formula weight	966.60	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 29.6458(13) Å	α= 90°.
	b = 15.9690(7) Å	β= 98.420(2)°.
	c = 18.0186(8) Å	γ = 90°.
Volume	8438.3(6) $Å^3$	
Z	8	
Density (calculated)	1.522 Mg/m^3	

Absorption coefficient	0.690 mm^{-1}
F(000)	3984
Crystal size	0.100 x 0.100 x 0.100 mm^3
Theta range for data collection	2.56 to 25.35°.
Index ranges	-35<=h<=35, -19<=k<=19, -21<=l<=21
Reflections collected	40419
Independent reflections	7684 [R(int) = 0.0674]
Completeness to theta = 25.00°	99.3 %
Absorption correction	Multiscan
Max. and min. transmission	1.0000 and 0.9357
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7684 / 4 / 549
Goodness-of-fit on F^2	1.198
Final R indices [I>2sigma(I)]	R1 = 0.0388, wR2 = 0.0921
R indices (all data)	R1 = 0.0395, wR2 = 0.0924
Largest diff. peak and hole	0.532 and -0.676 $e.Å^{-3}$

9. References

1. H. W. Gibson, S. H. Lee, P. T. Engen, P. Lecavalier, J. Sze, Y. X. Shen, M. Bheda, *J. Org. Chem.* **1993**, *58*, 3748-3756.
2. V. Aucagne, K. D. Hänni, D. A. Leigh, P. J. Lusby, D. B. Walker, *J. Am. Chem. Soc*. **2006**, *128*, 2186-2187.