Electronic Supplementary Informations

Nicolas Zigon, Patrick Larpent, Abdelaziz Jouaiti,Nathalie Kyritsakas and Mir Wais Hosseini

Molecular Tectonics Laboratory (UMR 7140)

University of Strasbourg

Institut Le Bel, 4 rue Blaise Pascal, 67000 Strasbourg, France

Tel: +33 3 68 85 13 23

Fax: + 33 3 68 85 13 25

E-mail: hosseini@unistra.fr

I - Experimental procedures

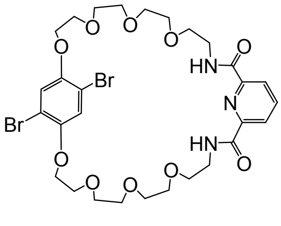
Analytical solvents were purchased at analytical grade and used without further purification. Every commercially available product was used as received without further purification.

^1H and ^{13}C spectra were recorded at 298 K on either a Bruker AV300, AV400, AV500 or AV600 spectrometers, with the solvent peak as the internal reference. In the assignment, the chemical shift is given first, followed in brackets by the multiplicity of the signal (br = broad, m = multiplet, s = singulet, d = doublet, t = triplet), the integration, the assignment and the coupling constants. Mass spectrometry was performed by the Service de Spectrométrie de Masse, University of Strasbourg. Elemental analyses were performed by the Service de Microanalyses, University of Strasbourg. UV-visible spectra were recorded on a Perkin Elmer Ubikon XL spectrometer. Wavelengths and molar extinction coefficients are respectively displayed in nm and $L\cdot mol^{-1}\cdot cm^{-1}$. Luminescence spectra were acquired on a Perkin Elmer LS55 spectrometer or a HORIBA JobinYvon Fluorolog FL3-22, at ambient temperature in aerated solutions. X-Ray diffraction studies on single crystals were performed on a Bruker APEX8 CCD Diffractometer equipped with an Oxford Cryosystem liquid N_2 device, at 173(2) K, using graphite-monochromated Mo-Kα (λ= 0.71073 Å) 50 radiation. For both structures, diffraction data were corrected for absorption. The Structures was solved using SHELXS-97 and refined by full matrix least-squares on F^2 using SHELXL-97.[1]

Luminescence quantum yields (Φ_{em}) were measured on optically dilute solutions (absorbance value lower than 0.1 at excitation wavelength). Quantum yields were determined relative to those of quinine sulfate (0.54 in 0.1M H_2SO_4).[2] The lifetimes of the compounds were recorded on the HORIBA JobinYvon Fluorolog FL3-22 spectrometer using a USHIO short arc lamp with a 450 W xenon tube. The single-photon-counting detector was a HORIBA JobinYvon TBX-4, and data analysis was performed using the commercially available Datastation and DAS6 software (HORIBA Jobin Yvon IBH).

Compound **2** was synthesized as previously described.[3]

Compound 3:

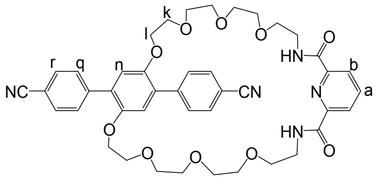


To a degassed DMF solution (350 mL) of dimesylate **2** (1.2 g, 1.8 mmol, 1 eq.), 2,6-dibromohydroquinone (0.48 g, 1.8 mmol, 1 eq.) and Cs_2CO_3 (2.34 g, 7.2 mmol, 4 eq.) were successively added. The reaction mixture was heated at 90 °C for 20 h before it was allowed to reach RT. The solvent was then removed under reduced pressure and the resulting solid was suspended in CH_2Cl_2 (150 mL), washed with H_2O (100 mL) and 10 % NH_4Cl (2 x 100 mL). After drying of the organic phase over $MgSO_4$ and evaporation of the solvent, the residue was purified by filtration column (SiO_2, CH_2Cl_2/MeOH 95/5) affording **3** as an orange oil (1.2 g, 1.6 mmol, 90 %).

^{1}H-NMR (CD_2Cl_2, 300 MHz): δ (ppm) = 3.51-3.65 (m, 24H, OCH_2), 3.77 (m, 4H, OCH_2), 4.16 (m, 4H, OCH_2), 7.25 (s, 2H, Ar), 7.99 (dd, 1H, pyr, ^3J = 7.9 Hz), 8.26 (d, 2H, pyr, ^3J = 7.9 Hz), 8.27 (br, superimposed with the signal at 8.26 ppm, 2H, NH).

^{13}C-NMR (CD_2Cl_2, 75 MHz): δ (ppm) = 39.8, 70.1, 70.3, 70.6, 70.8, 70.9, 70.9, 71.4, 111.7, 120.0, 125.0, 139.2, 149.5, 150.8, 163.9.

Compound 1:



Compound **3** (347 mg, 0.46 mmol, 1 eq.) was dissolved in toluene (10 mL), 4-pyridylboronic acid (205 mg, 1.39 mmol, 3 eq.) in MeOH (5 mL) and an aqueous solution of Na_2CO_3 (2 M, 6 mL) were added and the mixture was degassed before addition of $Pd(PPh_3)_4$ (100 mg, 0.09 mmol, 0.2 eq.). The biphasic mixture was heated at 80 °C for 20 h. The solvents were removed, the resulting solid was partitioned between CH_2Cl_2 (100 mL) and a 10 % $NaHCO_3$ solution (100 mL) and the organic phase was further washed with a 10 % $NaHCO_3$ solution (2 x 100 mL), dried over $MgSO_4$ and evaporated to dryness. Column chromatography (SiO_2, CH_2Cl_2/MeOH 100/0 to 97/3) afforded the desired compound **1** as a yellow solid (0.25 g, 0.31 mmol, 68 %).

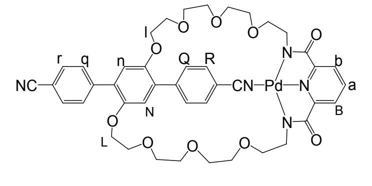
^{1}H-NMR (CD_2Cl_2, 500 MHz): δ (ppm) = 3.46-3.60 (m, 24H, OCH_2), 3.69 (m, 4H, H_k), 4.17 (m, 4H, H_l), 7.15 (s, 2H, H_n), 7.77 (d, 4H, H_r, ^3J = 8.5 Hz), 7.84 (d, 4H, H_q, ^3J = 8.5 Hz), 8.00 (t, 1H, H_a, ^3J = 7.8 Hz), 8.26 (d, 2H, H_b, ^3J = 7.8 Hz), 8.39 (br, 2H, NH).

^{13}C-NMR (CD_2Cl_2, 125 MHz): δ (ppm) = 39.7, 70.0, 70.0, 70.4, 70.5, 70.6, 70.9, 71.1, 110.8, 117.1, 119.8, 124.9, 130.3, 130.8, 132.3, 139.2, 143.1, 149.4, 150.9, 163.9.

UV-Vis (CH_2Cl_2): λ_{max} (log ε) = 251 (4.43), 284 (4.44), 347 (4.17).

MS (ESI): m/z calcd for $C_{43}H_{47}N_5O_{10}Na^+$ $[M + Na]^+$ 816.32 g·mol^{-1}; found 816.33 g·mol^{-1}.

Compound 1-Pd:



The compound **1** (21 mg, 26.4 μmol, 1 eq.) was dissolved in CH_2Cl_2/CH_3CN (1/1, 5 mL) and a solution of $Pd(OAc)_2$ (7 mg, 31.1 μmol, 1.2 eq.) in CH_3CN (5 mL) was added dropwise.

After 2 h. at RT, the solution was evaporated to dryness and column chromatography (SiO_2, CH_2Cl_2/MeOH 95/5) afforded **2**-Pd quantitatively as a yellow solid.

^{1}H-NMR (CD_2Cl_2, 500 MHz): δ (ppm) = 3.57-3.81 (m, 28H, OCH_2), 4.21 (m, 2H, H_l), 4.29 (m, 2H, H_L), 6.93 (s, 1H, H_n), 7.66 (d, 2H, H_{b+B}, ^3J = 7.8 Hz), 7.69 (d, 2H, H_r, ^3J = 8.5 Hz), 7.73 (d, 2H, H_q, ^3J = 8.5 Hz), 7.84 (s, 1H, H_N), 8.04 (t, 1H, H_a, ^3J = 7.8 Hz), 8.08 (d, 2H, H_R, ^3J = 8.5 Hz), 8.22 (d, 2H, H_Q, ^3J = 8.5 Hz).

^{13}C-NMR (CD_2Cl_2, 125 MHz): δ (ppm) = 46.4, 46.4, 69.4, 70.1, 70.5, 70.7, 70.8, 70.9, 71.0, 71.1, 71.4, 71.4, 71.5, 71.6, 71.7, 72.5, 106.3, 111.2, 115.4, 119.3, 120.0, 124.0, 124.9, 128.9, 130.5, 130.8, 131.3, 132.2, 134.1, 141.4, 143.0, 145.4, 151.2, 151.7, 153.3, 153.4, 170.5, 170.7.

UV-Vis (CH_2Cl_2): λ_{max} (log ε) = 296 (4.55), 354 (4.37).

MS (ESI): m/z calcd for $C_{43}H_{46}N_5O_{10}Pd^+$ $[M + H]^+$ 898.23 g·mol^{-1}; found 898.23 g·mol^{-1}.

NMR studies:

In a NMR tube, the turnstile **1** was dissolved in CD_2Cl_2 (0.5 mL, C ≈ $5 \cdot 10^{-3}$ M). The effector (TBACN, DMAP, MsOH or NEt_3 solution in CD_2Cl_2) was added with a micro-syringe directly in the NMR tube and an NMR spectrum was acquired.

II - 2D-NMR ^{1}H-^{1}H NOESY spectra

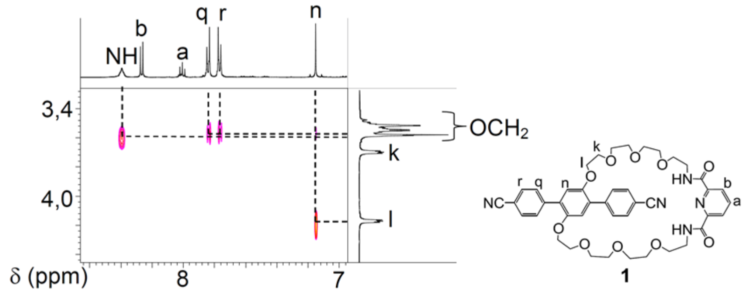


Figure S1: A portion of the NOESY spectra of **1** (CD_2Cl_2, 298 K, 500 MHz). In addition to correlations between H*n*/H*l* and H*NH*/H*e*, correlations between hydrogens H*q* and H*r* of the benzonitrile moieties and hydrogen atoms of the glycol chain are observed.

III - Luminescence spectra

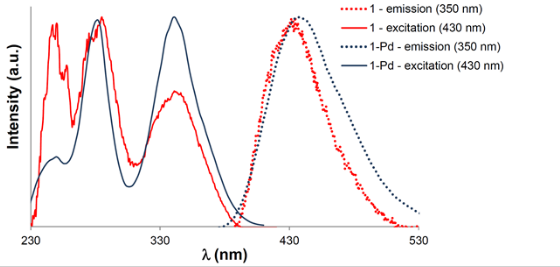
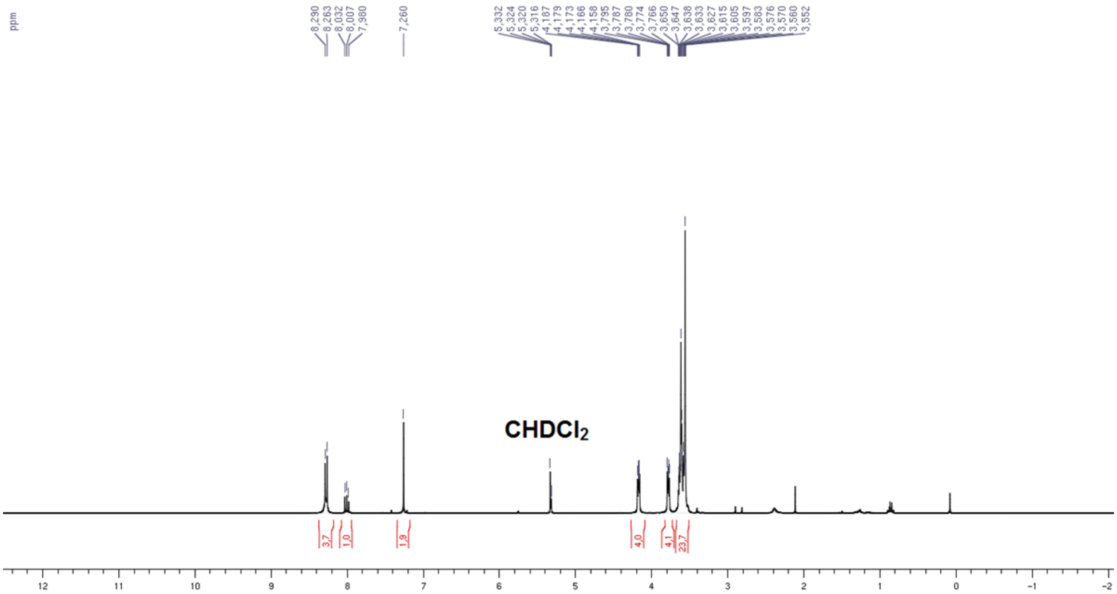


Figure S2 Normalized emission and excitation spectra (CH_2Cl_2, 298 K, aerated) for turnstiles **1** and **1**-Pd. The number inside of the brackets indicates either the excitation wavelength (for the emission spectra) or the reading wavelength (for the excitation spectra).

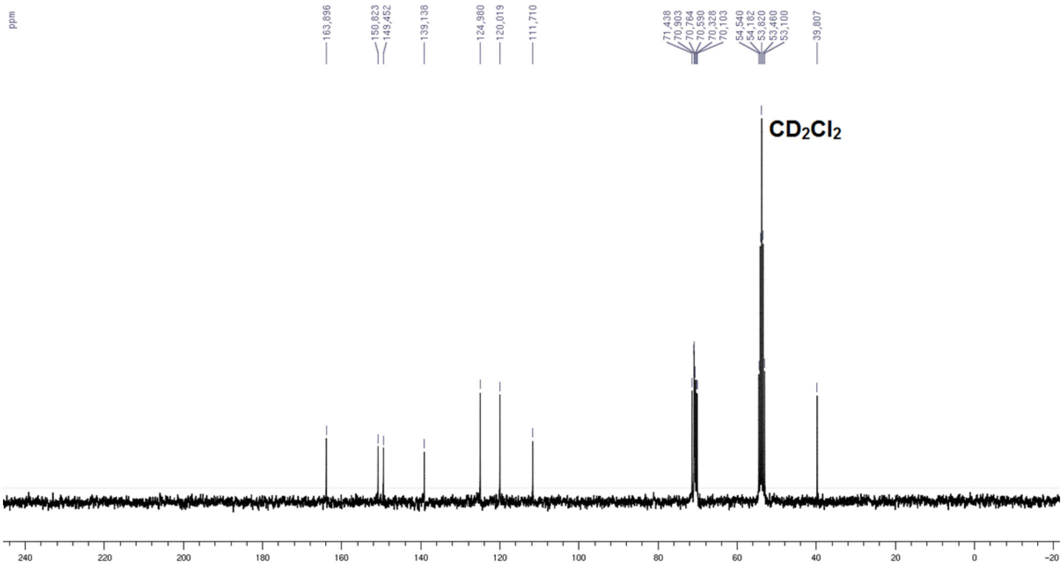
ID – 1D-NMR ^{1}H and ^{13}C spectra and mass spectra

Compound 4

^{1}H-NMR (CD_2Cl_2, 298 K, 300 MHz)

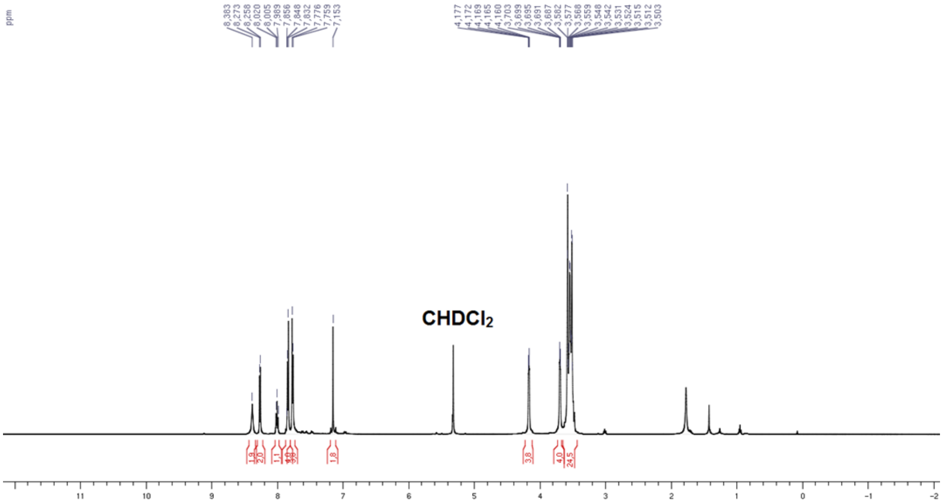


^{13}C-NMR (CD_2Cl_2, 298 K, 75 MHz)

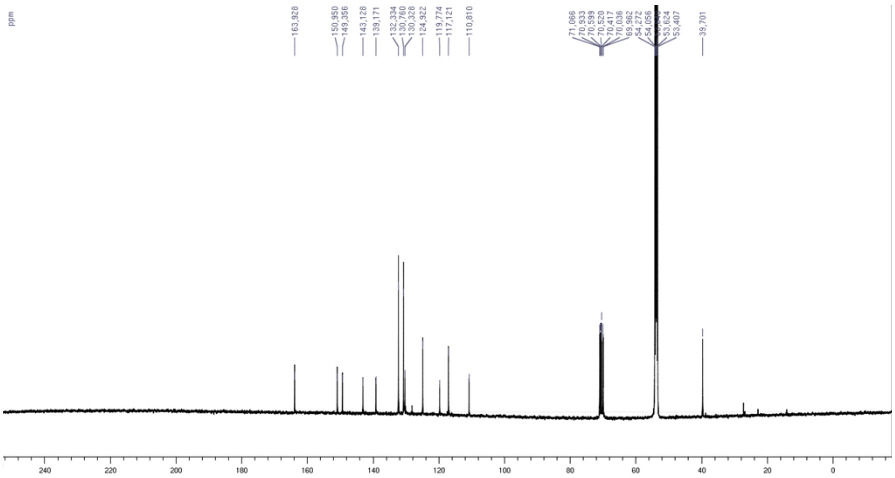


Compound 1

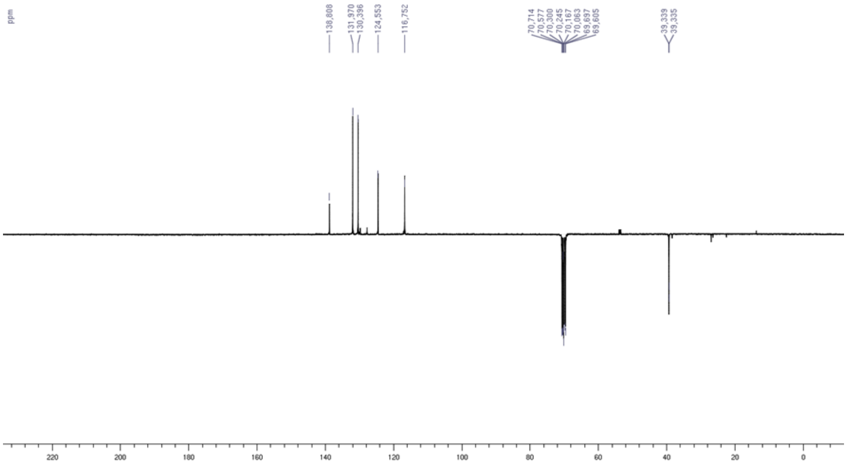
^{1}H-NMR (CD_2Cl_2, 298 K, 500 MHz)



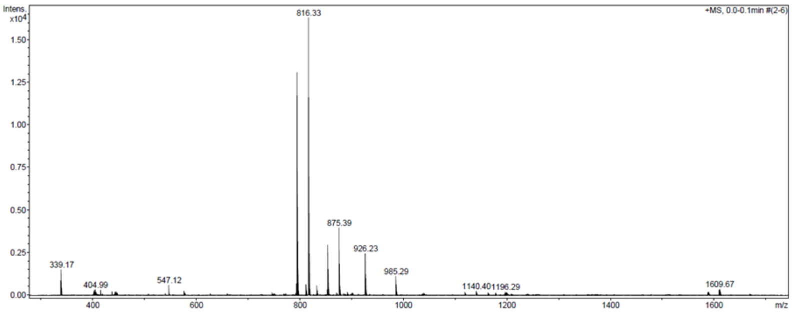
^{13}C-NMR (CD_2Cl_2, 298 K, 125 MHz)

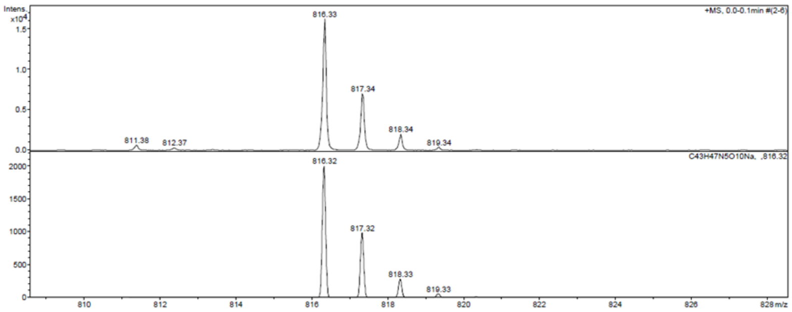


DEPT ^{13}C-NMR ($CDCl_3$, 298 K, 125 MHz)



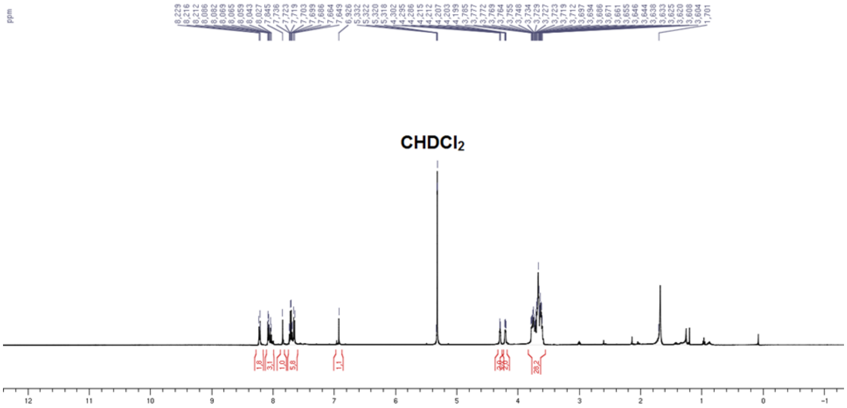
ESI MS



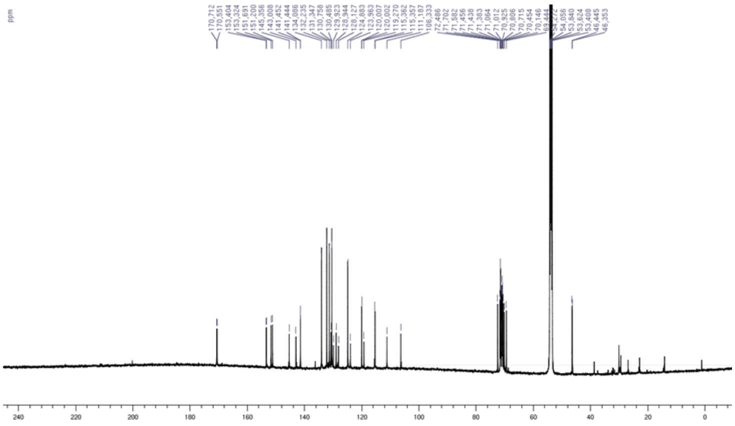


Compound 1-Pd

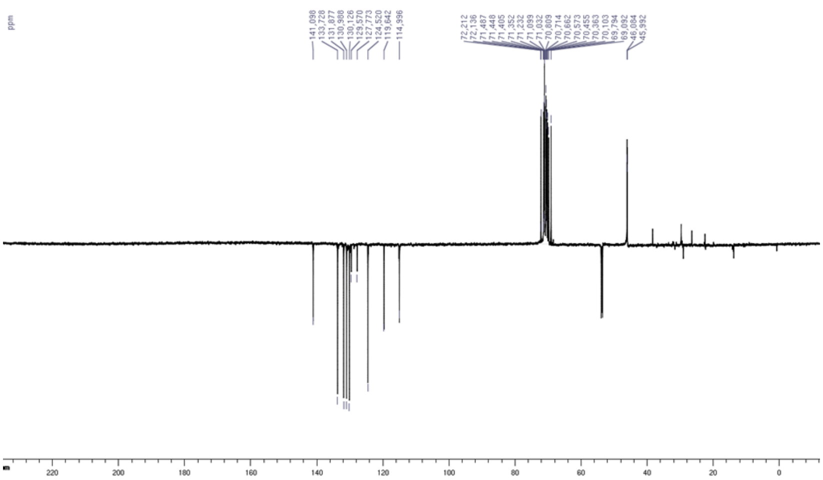
^{1}H-NMR (CD_2Cl_2, 298 K, 500 MHz)



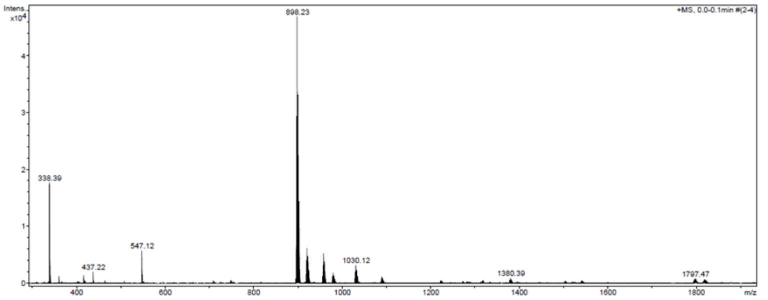
^{13}C-NMR (CD_2Cl_2, 298 K, 125 MHz)

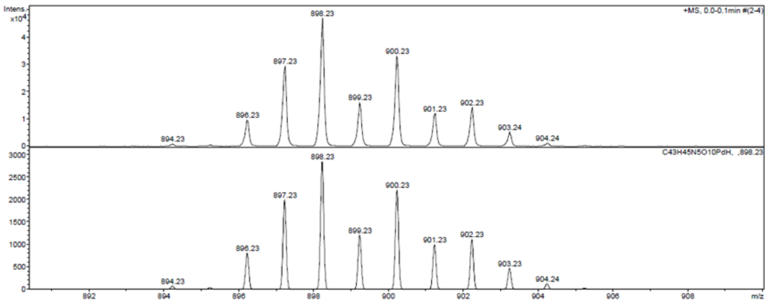


DEPT ^{13}C-NMR ($CDCl_3$, 298 K, 125 MHz)



ESI MS





V – Crystallographic data

Compound 1-Pd

Empirical formula	$C_{43}H_{45}N_5O_{10}Pd$	
Formula weight	898.24	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 8.4440(4) Å	α = 90°.
	b = 17.3203(6) Å	β = 95.788(2)°.
	c = 27.1664(11) Å	γ = 90°.
Volume	3952.9(3) $Å^3$	
Z	4	
Density (calculated)	1.509 Mg/m^3	
Absorption coefficient	0.537 mm^{-1}	
F(000)	1856	
Crystal size	0.06 x 0.05 x 0.05 mm^3	
Theta range for data collection	1.91 to 30.13°.	
Index ranges	-11<=h<=11, -24<=k<=19, -38<=l<=36	
Reflections collected	63826	
Independent reflections	11592 [R(int) = 0.1117]	
Completeness to theta = 30.13°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9737 and 0.9685	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11592 / 0 / 532	
Goodness-of-fit on F^2	0.993	
Final R indices [I>2σ (I)]	R1 = 0.0520, wR2 = 0.1190	
R indices (all data)	R1 = 0.1028, wR2 = 0.1416	
Largest diff. peak and hole	0.882 and -0.554 e.$Å^{-3}$	

References

[1] G. M. Sheldrick, *Program for Crystal Structure Solution*, (University of Göttingen), **1997**.

[2] W. H. Melhuish, *J. Phys. Chem.*, **1961**, *65*, 229-235.

[3] T. Lang, E. Graf, N. Kyritsakas, M. W. Hosseini, *Chem. Eur. J.*, **2012**, *18*, 10419-10426.