Coordination-driven self-assembly of polyoxometalates into discrete supramolecular triangles

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Electronic Supporting Information

Summary

Materials and Instrumentation

All available chemicals were purchased from Aldrich and used as received: isonicotinic acid, 2-amino-2-hydroxymethyl-propane-1,3-diol, thionyl chloride, triethylamine and *tert*-butylamine. Precursors were synthezised following published procedures: $TBA_3H_3[V_{10}O_{28}]$,[1] $PdCl_2(CH_3CN)_2$.[2] 3-Carboxyethyl-pyridine (3-pyCOOEt) was prepared *via* the acyl chloride, by treating isonicotinic acid in neat thionyl chloride at reflux, and subsequent treatment in absolute ethanol. Dry solvents and amines were kept in Schlenk flasks, under nitrogen, on activated molecular sieves.

Nuclear magnetic resonance (NMR) spectra were recorded in deuterated solvents at room temperatutre (r.t.) on Bruker AV spectrometers at 300, 400 or 500 MHz for ^{1}H NMR and at 75, 100 or 125 MHz for ^{13}C NMR (as stated in each case). Chemical shifts are reported in part per million (ppm) relative to TMS using residual solvent protons as reference (for example, 1.94 ppm for acetonitrile-d_3) and the carbon resonance of the solvent. PFG NMR experiments were conducted on Bruker AV spectrometer at 600 MHz maintaining the same conditions of temperature (r.t.=27°C), concentration (1×10^{-6} M) and viscosity (mixture of solvents CD_3CN/DMAc 3/2). This was confirmed by the observation of a constant diffusion coefficient for the solvent DMF, used as an internal reference: deviations of 5% are within the standard 10% deviations expected.

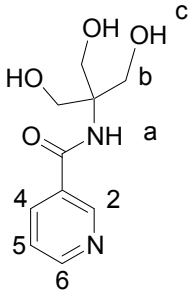
IR spectra were recorded using KBr pellets (unless otherwise stated) on a Perkin-Elmer Spectrum One FT-IR spectrometer, ranging from 500 to 4000 cm^{-1}. Relative intensities are given after the wavenumber as vs = very strong, s = strong, m = medium, w = weak, sh = shoulder, br = broad.

Accurate mass measurements were performed on a 6210 TOF mass spectrometer from Agilent technologies, coupled to a 1100 series LC system in negative or positive electrospray mode. Appropriate $[M]^{n-}$ or $[M]^{n+}$ species were used for empirical formula determination, and exact masses were calculated using Analyst® QS Software from Applied Biosystems and mMass Software.[3]

Crystallographic data sets for **2** were collected from single crystal samples (full details are available in the corresponding cif file) and were deposited at the Cambridge Crystallographic Data Centre, with deposition numbers CCDC 766600.

Synthesis and characterization

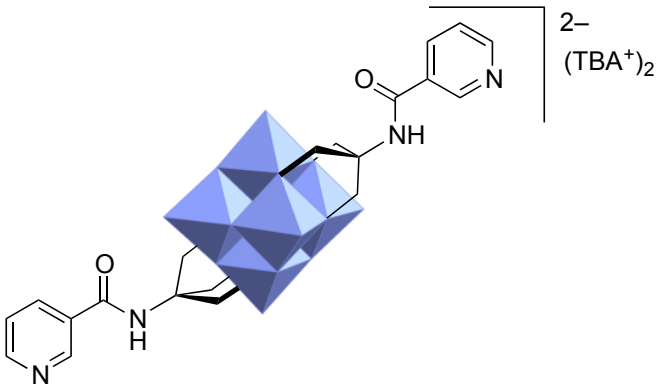
N-2((2-hydroxymethyl)-1,3-propanediol)-nicotinamid, 1



Following published procedure, 3-carboxyethyl-pyridine (3-pyCOOEt in the form of a brown oil*) (5.40 g, 32.2 mmol) was dissolved in dry DMSO (50 mL) before H_2N-$C(CH_2OH)_3$ (3.91 g, 32.2 mmol) and K_2CO_3 (4.45 g, 32.2 mmol) were added. The mixture was stirred under Ar for 16h at r.t. Insoluble K_2CO_3 was filtered off and the filtrate was concentrated to maximum (a few mL) under vacuum at 80-90°C. The resulting oil was triturated in DCM giving a yellowish paste. The paste was dissolved in minimum DCM/CH_3OH and purified by chromatography (SiO_2, gradient from pure DCM to DCM/CH_3OH 1/1). The obtained product was recrystallized in EtOH to give **1** (2.639 g, 36 %). ^{1}H NMR (d_6-DMSO, 400 MHz, 298 K): δ 8.96 (d, J = 2 Hz, 1H, H_2), 8.69 (dd, J = 5, 2 Hz, 1H, H_6), 8.14 (dd, J = 8, 2 Hz, 1H, H_4), 7.49 (m, 2H, H_5+ H_a), 4.70 (t, J = 6 Hz, 3H, H_c), 3.69 (d, J = 6 Hz, 6H, H_b). ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz, 298 K): δ 165.3 (*C*O), 151.1, 148.0, 134.7, 130.4, 122.8, 62.6 (*C*CH_2O), 59.5 (*C*H_2O). IR (KBr pellet, cm^{-1}): 2965 (ν C-H, m), 2870 (ν C-H, m), 1670 (ν C=O, vs), 1598 (s), 1584 (m), 1541 (vs), 1480 (w), 1465 (m), 1420 (m), 1338 (s), 1322 (s), 1292 (s), 1248 (m), 1196 (m), 1156 (m), 1125 (m), 1062 (vs), 1043 (vs), 1028 (vs), 977 (w), 880 (s), 714 (m), 670 (w), 633 (w), 612 (w), 472 (m). ESI-MS: $[M+H]^+$ calcd for $C_{10}H_{15}N_2O_4$ 227.1026; found 227.1027; $[M+Na]^+$ calcd for $C_{10}H_{14}N_2NaO_4$ 249.0846; found 249.0841. Anal. Calcd for $C_{10}H_{14}N_2O_4$: C, 53.09; H, 6.24; N, 12.38. Found: C, 52.50; H, 6.38; N, 12.21.

* we could see by NMR that the oil contained 20% DCM by integration, that could not be removed under vacuum overnight. This default of amine was calculated to give a real 1/1 stoichiometry reaction.

Lindqvist POM $TBA_2[C_{20}H_{22}N_4O_{21}V_6]$, 2·DMF



A Schlenk flask was charged with pyridine-triol **1** (0.610 g, 2.67 mmol), $TBA_3[H_3V_{10}O_{28}]$ (1.505 g, 0.89 mmol) and dry DMAc (31 mL). The orange mixture was heated in the dark at 85°C for 48h. The brown solution was filtered on a fine sintered glass filter upon cooling at r.t. and the resulting filtrate was added drop-wise to Et_2O (300 mL). The greenish precipitate was centrifugated and re-precipitated twice in a hot mixture of DMF: CH_3CN:Et_2O 2:1:6 (180 mL) to give an orange solid. After recristallization in DMF/Et_2O, **2·2DMF** was obtained as dark orange crystals suitable for X-ray measurement. Drying under vacuum afforded **2·DMF** (406 mg, 31%). ^{1}H NMR (CD_3CN, 400 MHz, 298 K): δ 8.91 (d, J = 2 Hz, 2H, H_2), 8.64 (dd, J = 5, 2 Hz, 2H, H_6), 8.07 (dd, J = 8, 2 Hz, 2H, H_4), 7.37 (dd, J = 8 Hz, 1 Hz, 2H, H_5), 6.54 (br, 2H, H_a), 5.40 (s, 12H, H_b), 3.08 (t, J = 8 Hz, 16H, -NCH_2-), 1.60 (m, 16H, -NCH$_2CH_2$-), 1.36 (m, 16H, -NCH$_2$CH$_2CH_2$-), 0.96 (t, J = 8 Hz, 24H, -NCH$_2$CH$_2$CH$_2CH_3$). ^{1}H NMR (d_6-DMSO, 400 MHz, 298 K): δ 8.93 (d, J = 2 Hz, 2H, H_2), 8.67 (dd, J = 5, 2 Hz, 1H, H_6), 8.15 (dd, J = 8, 2 Hz, 2H, H_4), 7.46 (dd, J = 8, 1 Hz, 2H, H_5), 5.28 (s, 12H, H_b), 4.71 (s, 2H, H_a), 3.17 (t, J = 8 Hz, 16H, -NCH_2-), 1.57 (m, 16H, -NCH$_2CH_2$-), 1.32 (m, 16H, -NCH$_2$CH$_2CH_2$-), 0.94 (t, J = 8 Hz, 24H, -NCH$_2$CH$_2$CH$_2CH_3$). IR (KBr pellet, cm^{-1}): 2961 (ν C-H, m), 2936 (ν C-H, m), 2872 (ν C-H, m), 1666 (ν C=O, vs), 1590 (m), 1544 (m), 1484 (δ C-H, m), 1458 (m), 1418 (w), 1383 (δ C-H, m), 1322 (m), 1286 (w), 1252 (w), 1187 (w), 1162 (w), 1103 (ν C-O, s), 1056 (ν C-O, s), 1031 (m), 953 (ν V=O, vs), 875 (w), 809 (ν V-O-V, s), 797 (ν V-O-V, s), 719 (ν V-O-V, vs), 649 (m), 582 (m), 513 (w). UV-visible (λ, nm (ε, M^{-1}·cm^{-1})): 250 (25.0), 353 (6.4). Anal. Calcd for $C_{55}H_{101}N_7O_{22}V_6$: C, 43.51; H, 6.71; N, 6.46. Found: C, 43.53; H, 6.13; N, 7.04.

Note: we could see the presence of a DMF solvent molecule by ^{1}H NMR.

ESI-Mass spectrometry

Composition	Formula	Simulated	Observed	Intensity
$[M]^{2-}$	$C_{20}H_{22}N_4O_{21}V_6$	479.8713	479.8722	5.25 x 10^5
$[M+TBA]^-$	$C_{36}H_{58}N_5O_{21}V_6$	1202.0267	1202.0256	2.2 x 10^5

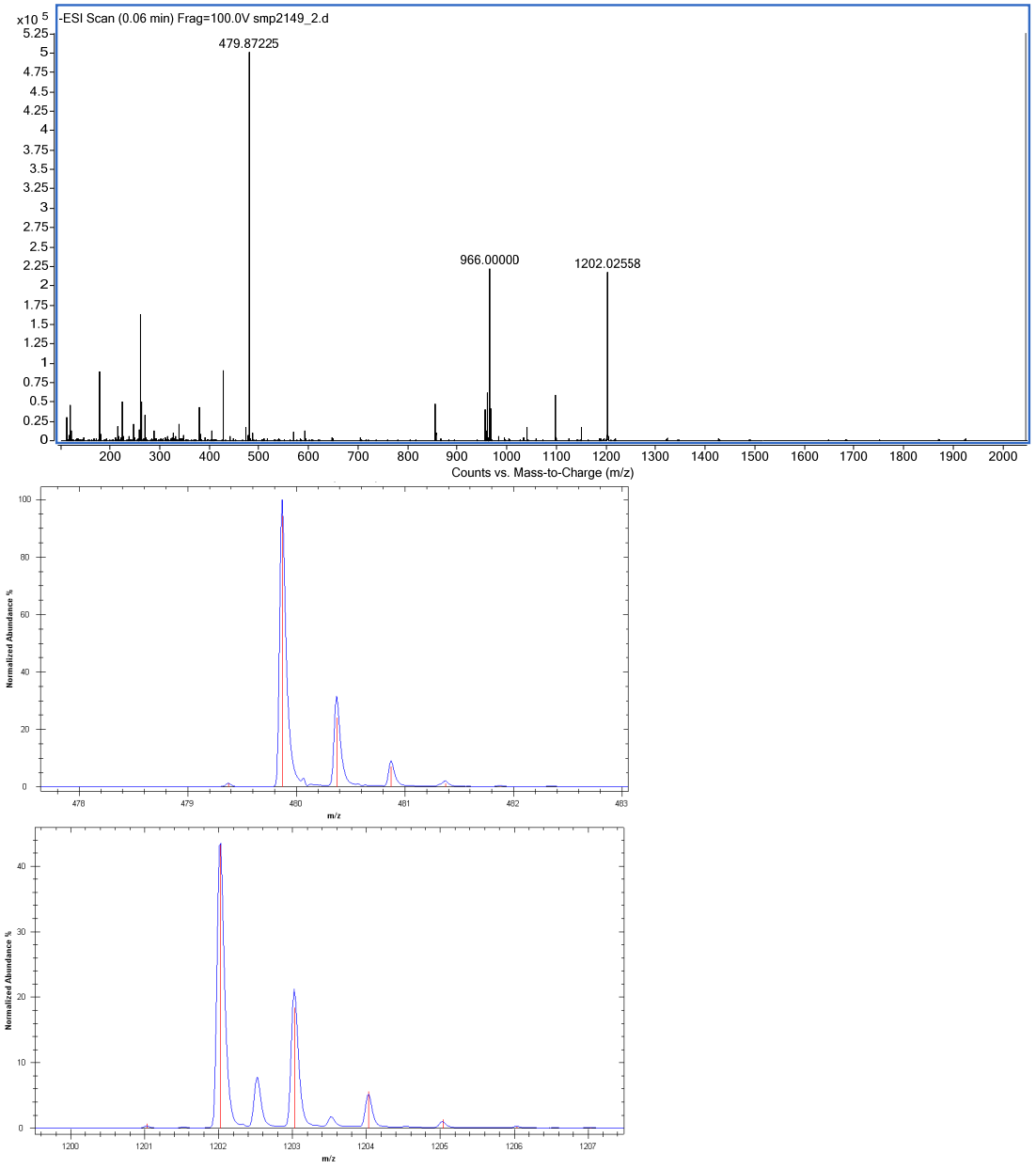


Figure 1. ESI-MS full spectrum for **2** (top) and isotopic distribution of the peaks for $[M]^{2-}$ at m/z = 479.8722 and for $[M+TBA]^-$ m/z = 1202.0256 (bottom), respectively (red: simulated; blue: experimental).

Crystallography

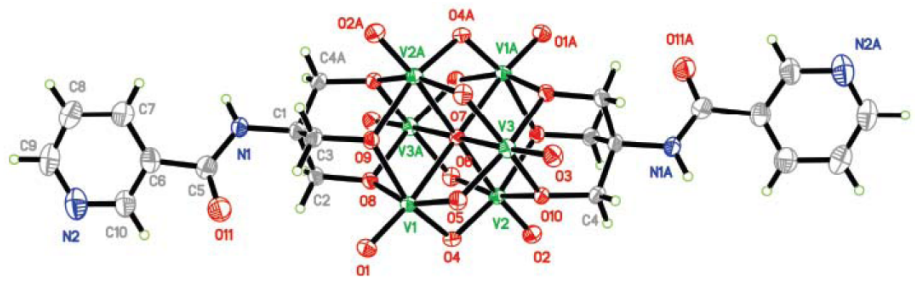


Figure 2. ORTEP diagram of **2** (thermal ellipsoids drawn at 50% probability), confirming the obtention of a *trans* bis-substituted POM building blocks with an angle of 60º between coordination vectors.

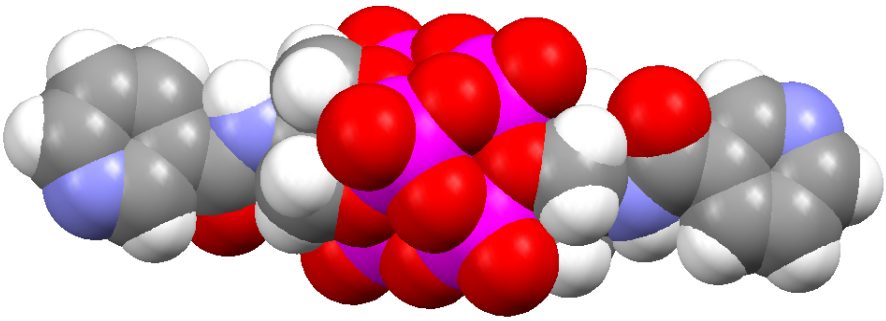
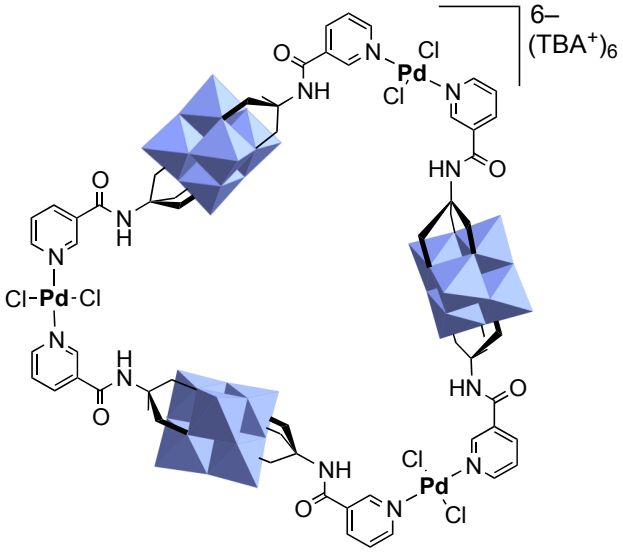


Figure 3. Space-fill diagram of **2**.

Table 1. Details of X-ray diffraction studies for **2**.

Compound	**Lindqvist POM 2**
Formula	$[C_{16}H_{36}N]_2[C_{20}H_{22}N_4O_{21}V_6]\cdot 2C_3H_7NO$
M_w (g/mol); F(000)	1591.16 ; 1668
T (K); wavelength (Å)	150 ; 0.71073
Crystal System	Monoclinic
Space Group	P21/c
Unit Cell: a (Å)	13.5535(17)
b (Å)	13.2675(17)
c (Å)	20.489(3)
β (°)	103.456(2)
V (Å^3); Z; $d_{calcd.}$ (g/cm^3)	3583.2(8) ; 2 ; 1.475
θ range (°); completeness	1.54 to 27.61 ; 0.984
collected reflections; R_σ	72395 ; 0.0403
unique reflections; R_{int}	8192 ; 0.073
μ (mm^{-1}); Abs. Corr.	0.828 ; Semi-empirical from equivalents
$R_1(F)$; w$R(F^2)$ [$I > 2\sigma(I)$]	0.0413 ; 0.1055
$R_1(F)$; w$R(F^2)$ (all data)	0.0605 ; 0.1160
GoF(F^2)	1.037
Residual electron density (e$^-$/Å^3)	0.871 and -0.451

Triangle $TBA_6[(2)_3(PdCl_2)_3]$, 3



Functionalized Lindqvist POM **2** (58 mg, 0.038 mmol) was dissolved in hot (80ºC) and dry DMAc (3 mL) before $PdCl_2(CH_3CN)_2$ was added (10 mg, 0.038 mmol). The mixture was heated in the dark at 80°C for 2 days. ^{1}H-NMR showed almost total conversion of **2**.

After cooling to r.t., the solution was filtered and added dropwise to diethyl ether (250 mL). The orange solid formed was centrifugated. After trituration in acetone and drying under vacuum, **3** is obtained as an orange microcristallin solid (31 mg, 17% isolated yield*). ^{1}H NMR (CD_3CN/DMAc, 400 MHz, 298 K): δ 9.1 (br, 2H, H_2), 8.8 (br, 2H, H_6), 8.4 (br, 2H, H_4), 8.1 (br, 2H, H_a), 7.6 (br, 2H, H_5), 5.4 (br, 12H, CH_2O), 3.1 (br, 16H, -NCH_2-), 1.6 (br, 16H, -NCH_2CH_2-), 1.4 (br, 16H, -$NCH_2CH_2CH_2$-), 1.0 (br, 24H, -$NCH_2CH_2CH_2CH_3$). Broadening of the signals is expected for two reasons: i) slower tumbling rate for the large assembly; ii) reduced flexibility of the organic ligand which can adopt two conformations with the carbonyl pointing inside or outside the ring. IR (KBr pellet, cm^{-1}): 2962 (ν C-H, m), 2933 (ν C-H, w), 2877 (ν C-H, m), 1666 (ν C=O, m), 1542 (m), 1470 (m), 1326 (m), 1280 (w), 1102 (ν C-O, s), 1054 (ν C-O, s), 955 (ν V=O, vs), 878 (w), 810 (ν V-O-V, s), 795 (ν V-O-V, s), 720 (ν V-O-V, s), 648 (w), 584 (m). Anal. Calcd for $C_{156}H_{282}N_{18}O_{63}Cl_6V_{18}Pd_3$: C, 38.50; H, 5.84; N, 5.18. Found: C, 38.07; H, 6.07; N, 4.84.

^{1}H NMR shows an almost quantitative conversion of starting POM **2** to **3**. However during the workup, especially on small scale, a lot of final product may be lost for two reasons: (i) the

concentration of the DMAc solution is quite low for an efficient precipitation of POM by addition of ether; (ii) some product stay stuck as a solid on frits, filters and sides of centrifugation tubes.

Mass spectrometry

Composition	Formula	Simulated	Observed	Intensity
$[(\mathbf{2})_3(PdCl_2)_3+TBA]^{5-}$	$C_{76}H_{102}N_{13}O_{63}Cl_6V_{18}Pd_3$	729.8070	729.7932	1.5×10^4
$[(\mathbf{2})_3(PdCl_2)_3+2TBA]^{4-}$	$C_{92}H_{138}N_{14}O_{63}Cl_6V_{18}Pd_3$	972.8299	972.8235	3.6×10^3
$[(\mathbf{2})_3(PdCl_2)_3+3TBA]^{3-}$	$C_{108}H_{174}N_{15}O_{63}Cl_6V_{18}Pd_3$	1377.8679	1377.8833	1.9×10^4

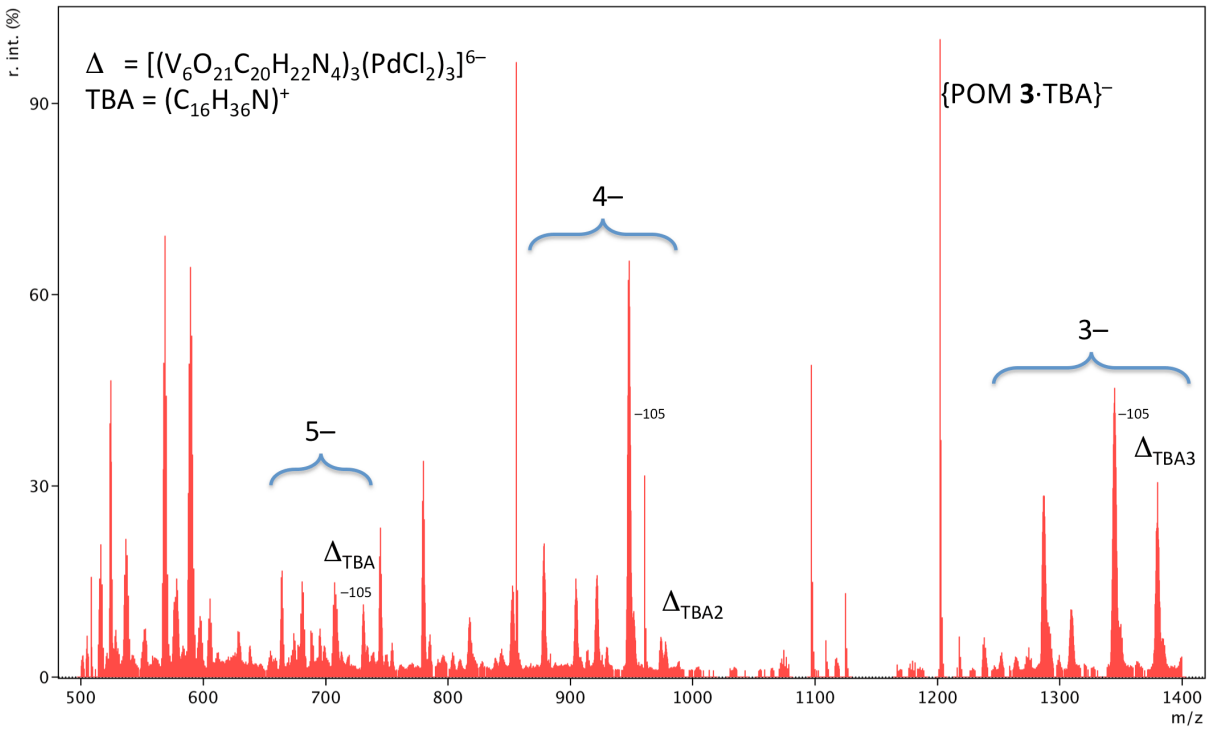


Figure 4. ESI-MS full spectrum for **3**.

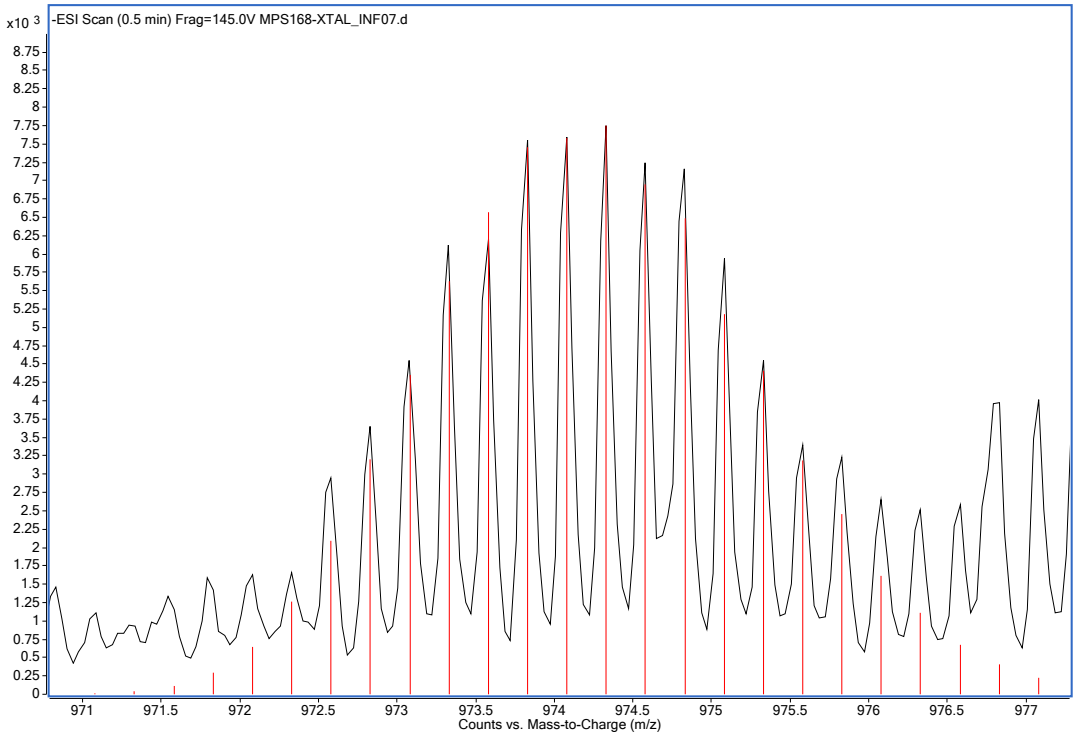


Figure 5. Isotopic distribution of the peak for $[M]^{2-}$ at m/z = 972.8235 (red: simulated; black: experimental) for triangle **3**.

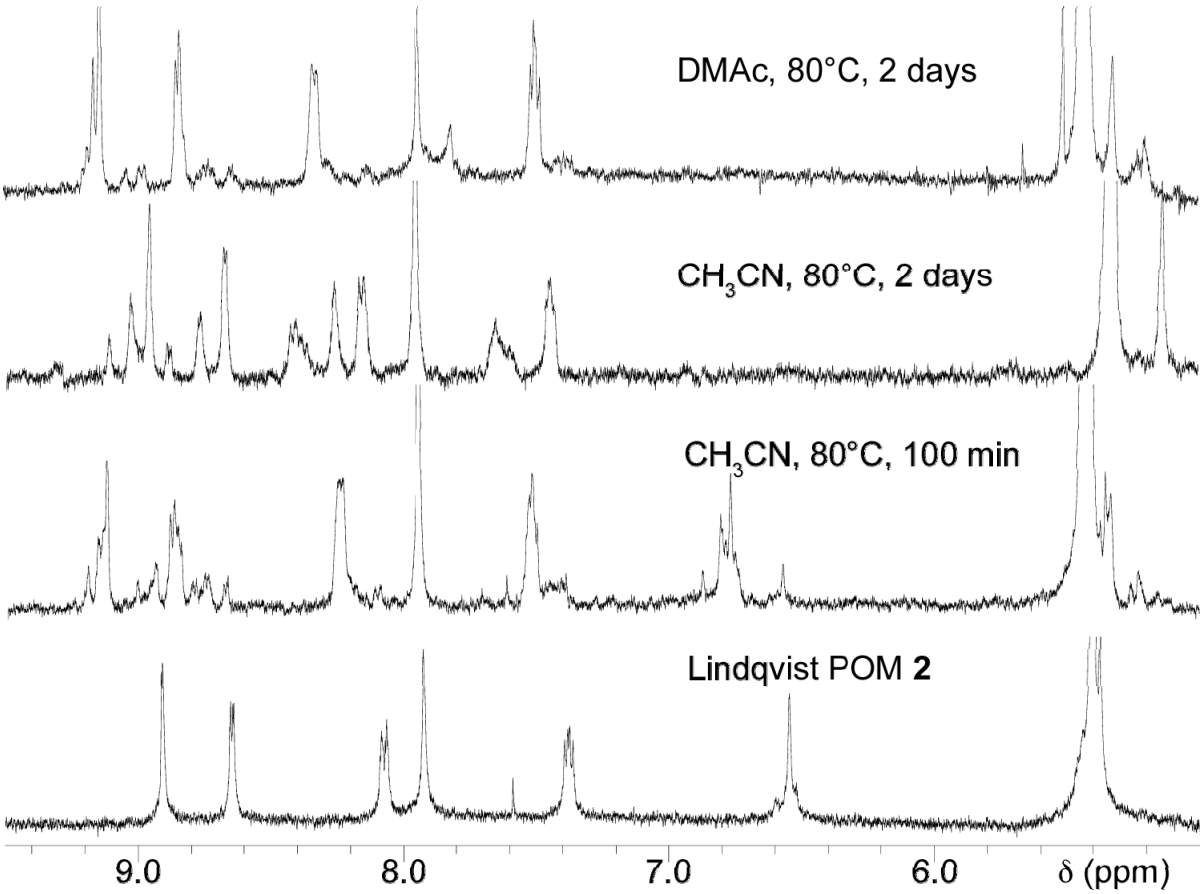


Figure 6. ^{1}H NMR monitoring (400 MHz, CD_3CN) of the formation of 3 in CH_3CN vs. DMAc: top, complexation in pure DMAc at 80˚C for 2 days; middle, complexation in pure CH_3CN at 80˚C for 100 min and for 2 days; bottom, ^{1}H NMR spectrum of 2 (starting POM) in CD_3CN. The complexation is more selective in DMAc with the formation of one set of pyridyl signals, typical of $\{(3\text{-py})_2PdCl_2\}$ motif, and disappearance of starting material **2**.

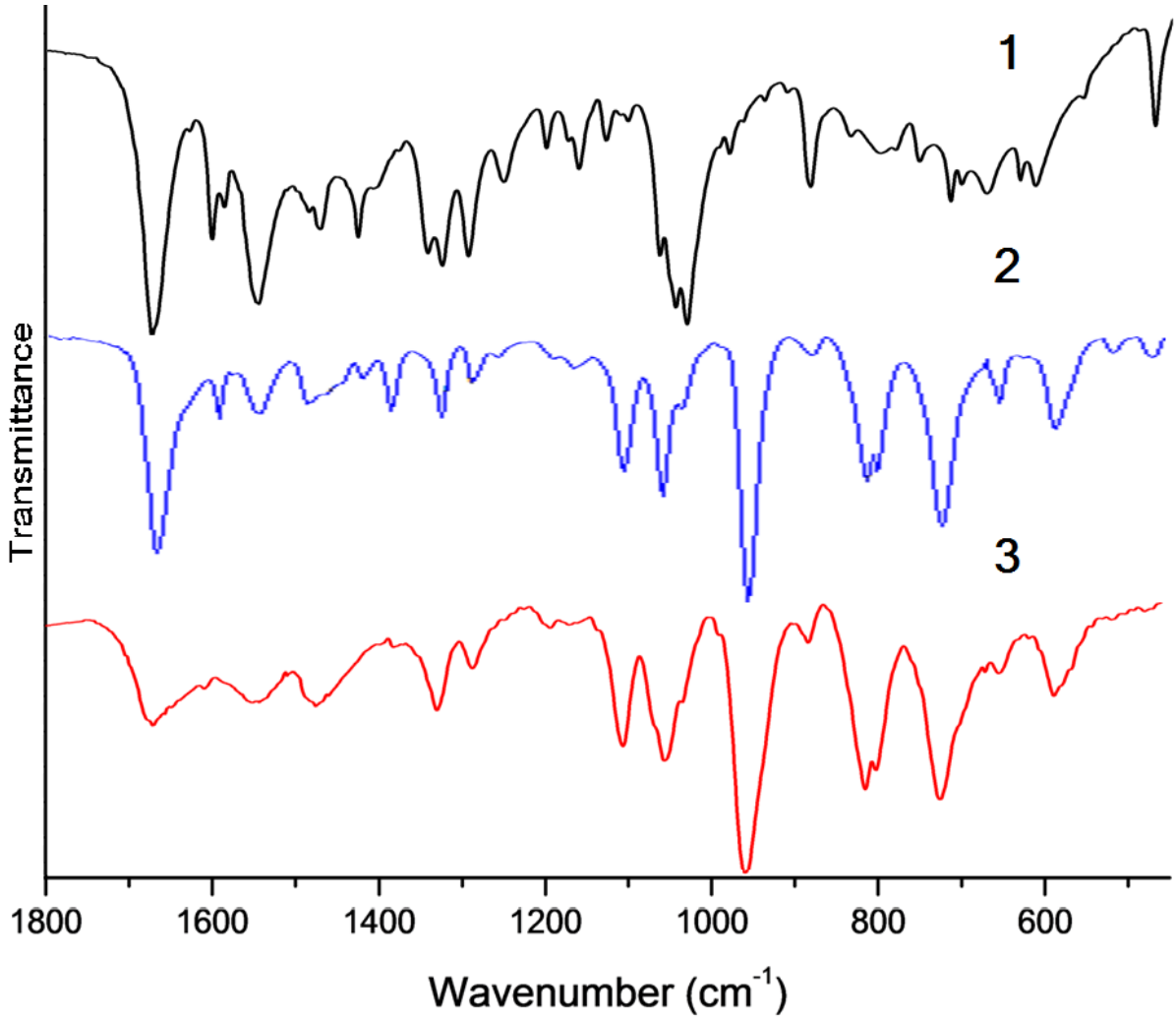
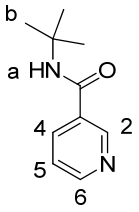


Figure 7. IR spectra for **1-3** (KBr pellet), between 1800 and 450 cm^{-1}.

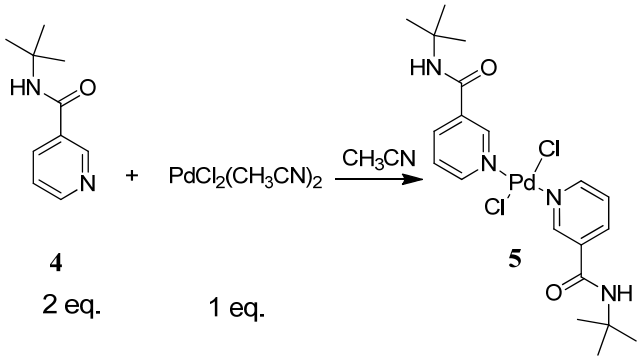
N-tert butylnicotinamid, 4



4

A 250 ml round-bottomed flask was charged with nicotinic acid (5.0 g, 40.6 mmol) and thionyl chloride (45 ml). The resulting slurry was refluxed under N_2 atmosphere for 18h to give a clear yellow solution. The solution was cooled to room temperature and the unreacted thionyl chloride was removed by distillation. The residue was dried for 2h under reduced pressure to give a pale yellow crystalline solid. To the same flask, dry DCM (100 mL) was added to give yellow slurry. The slurry was cooled down to 0 ^oC and *tert*-butylamine (5.9 g, 81.2 mmol) was added dropwise with stirring over half an hour under a flow of nitrogen to give pale yellow slurry. This slurry was refluxed for 2 h, under nitrogen. After 2 h, the mixture was cooled down to room temperature and filtered. The residue was washed with aqueous Na_2CO_3 solution (2x100 mL, pH ~ 8.3), followed by the washing with distilled water (3x50 mL). The residue was then dried overnight under vacuum to give **4** as a yellow solid (6.1 g, 84%). ^1H NMR ($CDCl_3$, 400 MHz, 298 K): δ 8.87 (s, 1H, H_2), 8.63 (d, J = 4 Hz, 1H, H_6), 8.02 (dd, J = 2, 8 Hz, 1H, H_4), 7.29 (m, 1H, H_5), 6.12 (s, 1H, H_a), 1.45 (s, 9H, H_b). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, 298 K): δ 165.1 (*C*O), 151.9, 147.9, 135.0, 131.6, 123.5, 52.1 (*C*CH_3), 28.9 (*C*H_3). UV-visible (λ nm, ε $M^{-1}\cdot cm^{-1}$): 210 (3.3), 255 (1.2). ESI-MS (low resolution): $[M+H]^+$ calcd for $C_{10}H_{15}N_2O$ 179.1; found 179.1. Anal. Calcd for $C_{20}H_{20}N_4O\cdot(H_2O)_{0.25}$: C, 71.30; H, 6.13; N, 16.63. Found: C, 71.13; H, 6.11; N, 16.79.

Dichloro-di(*N-tert*-butylnicotinamid)palladium(II), [(4)$_2$(PdCl$_2$)], 5



A solution of $PdCl_2(CH_3CN)_2$ (5mM; 76 µmol, 19.8 mg in 15.4 mL) was added dropwise to an acetonitrile solution of ligand **4** (5 mM; 1.02 equiv., 155 µmol, 27.6 mg in 31 mL) at r.t. Near the end of the addition, a precipitate started to form. The mixture was left stirring an additional 20 min before the solid was finally collected, washed with acetonitrile and dried under vacuum to give **5** (32.2 mg, 78%). ^1H NMR (CD_3CN/DMAc, 400 MHz, 298 K): δ 9.20 (s, 2H, H_2), 8.86 (d,

J = 6 Hz, 2H, H_6), 8.39 (d, *J* = 8 Hz, 2H, H_4), 8.28 (s, 2H, H_a), 7.57 (dd, *J* = 8, 6 Hz, 2H, H_5), 1.45 (s, 18H, CCH_3). Anal. Calcd for $C_{20}H_{28}Cl_2N_4O_2Pd$: C, 45.00; H, 5.29; N, 10.50. Found: C, 45.06; H, 5.31; N, 10.58.

Comparison of ^{1}H NMR

Table 2. Comparison of ^{1}H NMR chemical shifts of pyridyl groups. Note the similarities of uncomplexed ligands **2** and **4** and Pd complexes **3** and **5**.

	POM 2	**Triangle 3**	**Model ligand 4**	**Model Pd-complex 5**
H-2	8.91	9.1	8.87	9.20
H-4	8.07	8.4	8.02	8.39
H-5	7.37	7.6	7.29	7.57
H-6	8.64	8.8	8.63	8.86

Table 2 lists the chemical shifts of uncomplexed ligands **2** and **4** and their Pd complexes **3** and **5**. The chemical shifts for model complex **5** are very similar to those of triangle **3**, thus the coordination of two pyridyl groups on {$PdCl_2$} in **3** must be concluded. These two pyridyl groups coordinated to the Pd must belong to two different POMs **2** for obvious steric reasons.

References

[1] Day, V. W.; Klemperer, W. G.; Maltbie, D. J. *J. Am. Chem. Soc.* **1987**, 109, 2991.
[2] Noskowska, M.; Sliwinska, E.; Duczmal, W. *Transition Metal Chemistry* **2003**, 28, 756; an additional recrystallization in CH_3CN was performed to afford the desired compound.
[3] M. Strohalm, D. Kavan, P. Novak, M. Volny and V. Havlicek, *Anal. Chem.*, 2010, **82**, 4648-4651.