Supplementary Information

Design, synthesis and characterization of a Pt-Gd metal-organic framework containing potentially catalytically active sites

Kai C. Szeto,[†] Kjell Ove Kongshaug,[†,‡] Søren Jakobsen,[†] Mats Tilset,[§,*] and Karl Petter Lillerud[†]

Centre for Materials Science and Nanotechnology, University of Oslo, P.O. Box 1126 Blindern, N-0318 Oslo, Norway, and Centre for Theoretical and Computational Chemistry, Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo, Norway.
e-mail of corresponding author: mats.tilset@kjemi.uio.no

[†] Centre for Materials Science and Nanotechnology.
[‡] Current address: Norwegian Defence Research Establishment, P.O. Box 25, NO-2027 Kjeller, Norway.
[§] Centre for Theoretical and Computational Chemistry.

Supplementary Information S1. TGA of the [BPDC]$PtCl_2$ complex (1).

The melting point of **1** ([BPDC]$PtCl_2$, BPDC = 2,2’-bipyridine-5,5’-dicarboxylate) could not be clarified by standard procedure for organic molecules, caused by the high thermal stability. The temperature of decomposition was determined by TGA. 9.22 mg of the sample was placed in an Al_2O_3 crucible and heated from room temperature to 1000 °C (heating rate: 5°C/min) with a continuous flow of N_2 (15 ml/min). The TG-pattern is depicted in Fig. S1.

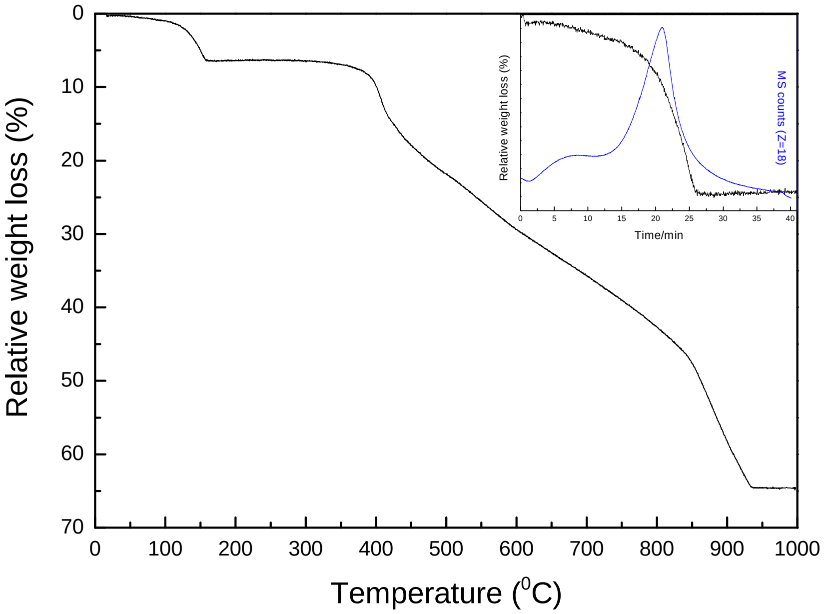

Fig. S1: Decomposition of **1** followed by TGA. The inset reports the TG-MS data.

The first weight loss around 100 °C fits to 2 water molecules per [BPDC]$PtCl_2$ molecule (observed: 6.39%, calculated: 6.60%). The inset of Fig. S1 reports the TG-MS analysis around the first weight loss (TG-curve in black and MS-curve in blue). A separate OmniStar GSD300 O mass spectrometer was connected to the TGA furnace through a stainless steel capillary. The tip of the capillary was placed just above the sample. Only signals from mass number 17 and 18 were observed to increase. The signal ratio between m_{17}/m_{18} is constantly about 0.26 and strongly suggests that water is the leaving component.

The next weight loss extends from 350 °C to 940 °C. This region corresponds to decomposition of the organic part and chloride in the complex (observed: 58.18%, calculated: 57.70%). The final residue is metallic platinum (observed: 35.43 % left, calculated: 35.71 %).

Supplementary Information S2. Studies of coordination polymer (2) by microscopy.

A light microscope image of the isolated product (Fig. S2) shows presence of at least two different phases in the isolated product synthesized by method 1 (described in the article). Peaks in the powder X-ray pattern can easily be assigned to 2,2'bipyridine-5,5'-dicarboxylic acid (the ligand) and the coordination polymer **2** ($\{[(BPDC)PtCl_2]_3(Gd(H_2O)_3)_2\}\cdot5.5H_2O$).

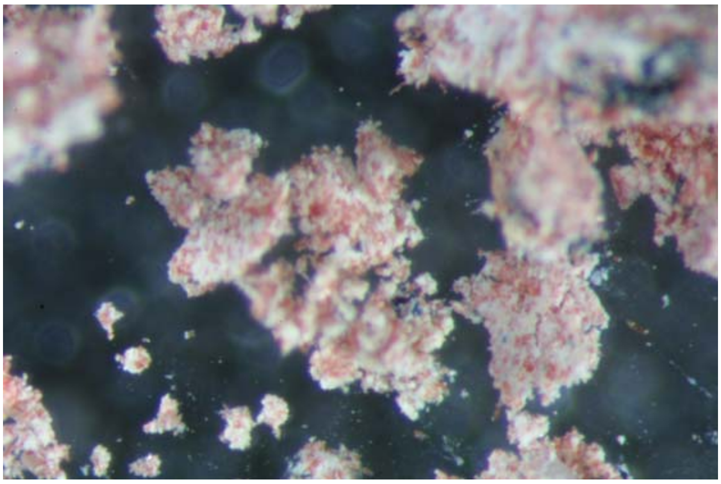

Fig. S2: Digital image of the isolated product synthesized in a stainless steel autoclave.

Thus, the white powder on Fig. S2 is the un-reacted ligand while the red compound is **2**. Analysis in SEM indicates that single crystals of the new phase are present (Fig. S3).

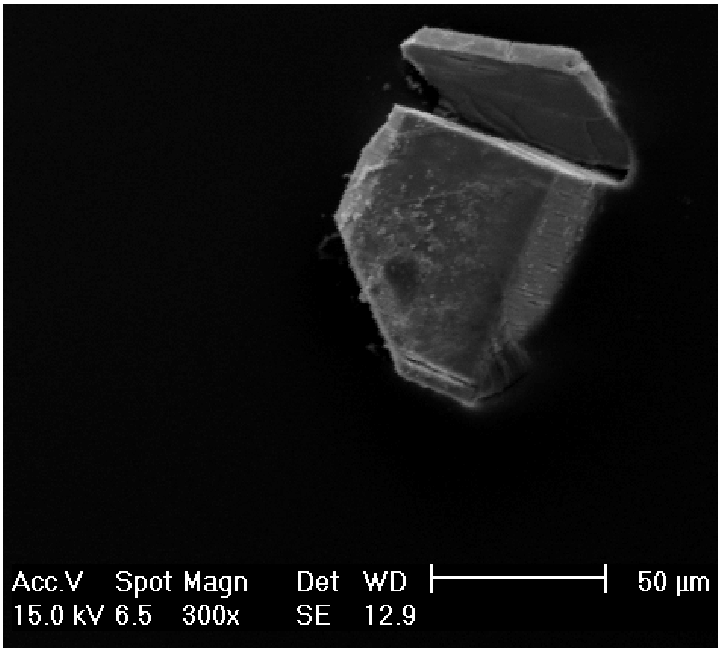

Fig. S3: SEM image of a crystal.

Supplementary Information S3. X-ray diffraction patterns for coordination polymer (2).

Powder X-ray diffraction (XRD) data are recorded in a Bruker AXS D5000 diffractometer in Bragg-Brentano geometry. The diffractometer is equipped with Cu-tube, single Ge-monocromator (λ=1.540598 Å) and PSD (position sensitive detector). All patterns without further description are collected at room temperature in air.

The sample was deposited on a flat sample holder of glass. The pattern was collected with a step size of 0.015° (2θ-range) and 1 second exposure per step.

The experimental powder X-ray diffraction (XRD) pattern is compared with the simulated pattern from single crystal data in Fig. S4.

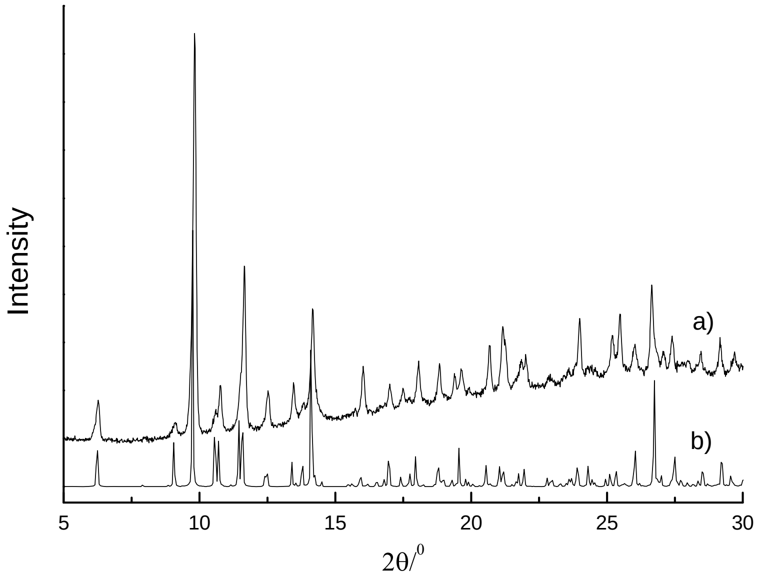

Fig. S4: Observed (a) and simulated (b) XRD pattern of **2**.

Compound **2** can be synthesized by different methods as discussed in the article. Each method gives different quality of the product, their XRD patterns are shown in Fig. S5. The product synthesized in an oven with slow heating rate forms a multi-phase system (pattern a), including single crystal of **2**. Due to an orientation effect of the sample, the intensity distribution may be different. Performing the synthesis with fast heating rate in a microwave oven results a crystalline powder (pattern b). The XRD pattern of **2** synthesized after mixing **1** and $Gd(NO_3)_3\cdot 6H_2O$ is denoted as c) in Fig. S5. The peak positions remain on the same places as pattern b. However, the peaks are broader which indicate that the product is less crystalline or has a relative small particle size.

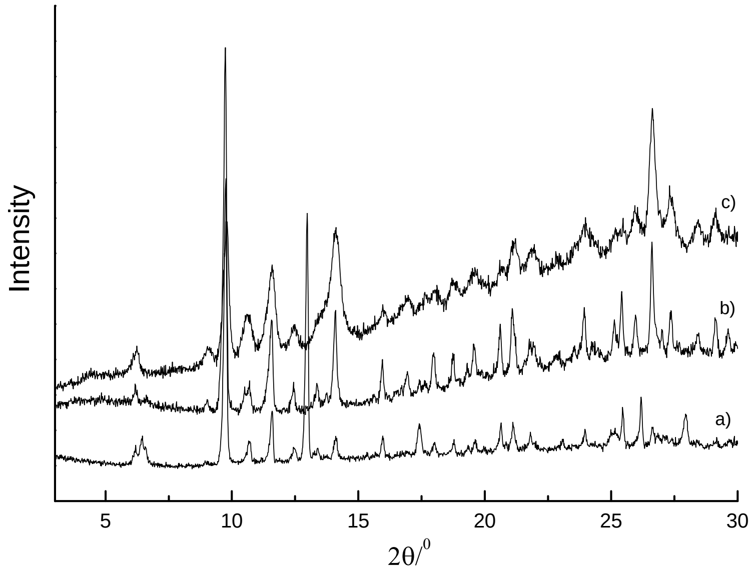

Fig. S5: X-ray patterns of **2** synthesized by different methods.

Supplementary Information S4. Stability of coordination polymer (2).

The TGA pattern of **2** in O_2 atmosphere (red curve) is depicted in Fig. S6. The heating rate was 10 °C/min. The sample (12.57 mg) was placed in an Al_2O_3 crucible with a continuous flow (15 ml/min) of O_2 during the analysis. The corresponding experiment in N_2 atmosphere (taken from the article) is again given (as the blue curve) for comparison. The results show that **2** are stable under both inert and oxidizing conditions.

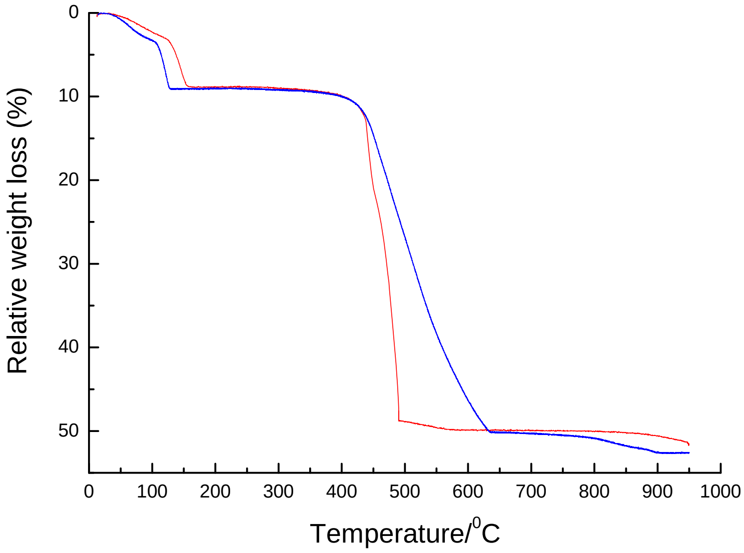

Fig. S6: TGA analysis of **2** in N_2 (blue curve) and O_2 (red curve) atmosphere.

Fig. S7 shows the powder X-ray patterns from the same synthesis batch of **2** (synthesized by method 1) recorded after some hours (curve a), one year (curve b) and two years (curve b) after the product was isolated. The powder X-ray patterns confirm that the sample is still crystalline after years and the structure is stable. The compound has in the mean time been stored in a closed colorless glass tube at normal atmosphere and ambient temperature without further protection of light and moisture.

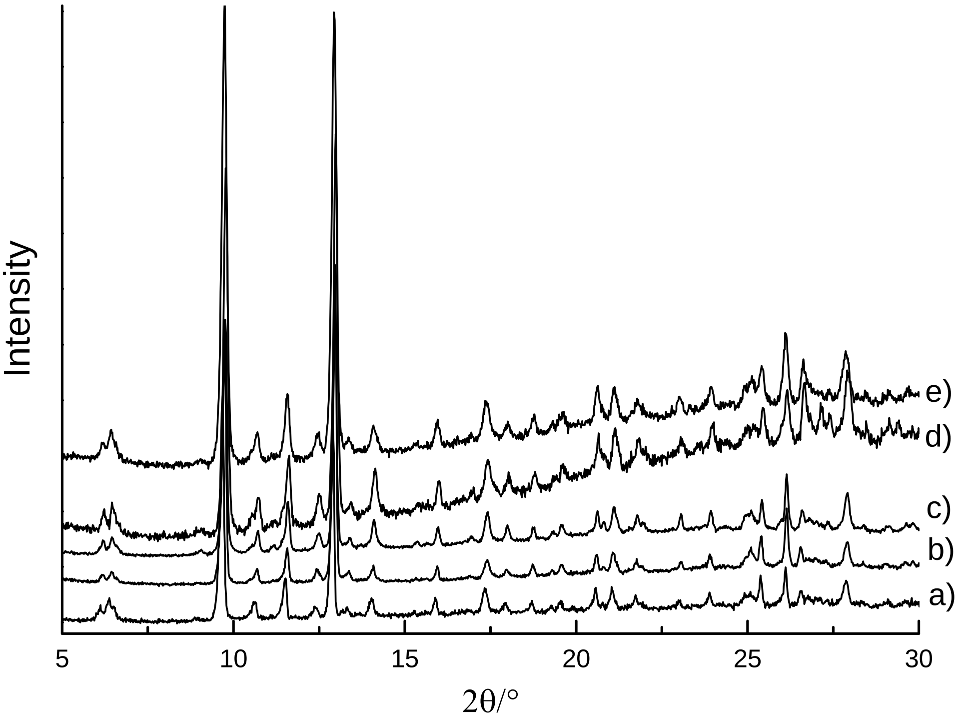

Fig. S7: Powder X-ray patterns of **2** taken after some hours (a), 1 year (b), 2 years (c), 3 years (d), and 4 years (e) after the product was isolated.

Supplementary Information S5. Solvent removal from the structure followed by TG-MS.

The composition of the exhaust during a TGA can be identified by connecting a MS to the system (TG-MS). A separate OmniStar GSD300 O mass spectrometer is connected to the TGA furnace through a stainless steel capillary. The tip of the capillary is located above the Al_2O_3 sample holder. The sample is then heated to 220 °C (heating rate: 5 °C/min) with continuously flow of N_2. The result is illustrated in Fig. S8 and confirms that water is leaving at the first weight loss in the TGA.

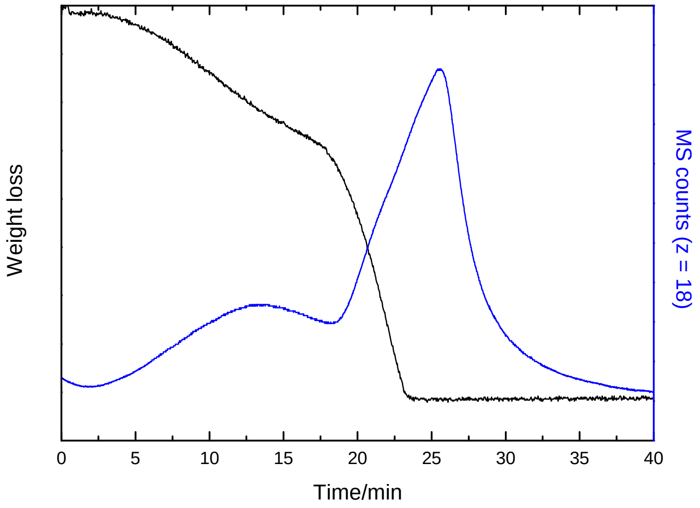

Fig. S8: TG-MS results. The weight loss is represented by the black curve and the blue curve is the MS counts of mass number 18 (corresponds to water).