Experimental 1. Preparation of complex 2, 3 and 4.

**Figure 1.** Coordination geometry around the metal centers in 2-4.

**Figure 2.** Three fold interpenetrated PtS network of complex 2 generated from tetrahedral organic linker 1 and Zn₂ paddle-wheel clusters.

**Figure 3.** Two interpenetrated Adamantanoid network of complex 3 generated with trapped solvent molecules.

**Figure 4.** Two-fold interpenetrated Lonsdaleite network of complex 4 generated from tetrahedral building block, 1 and Zn2 clusters.

**Figure 5-7.** Thermal analysis of 2-4.

**Figure 8.** Variable temperature PXRD of the complex 2 using Cobalt radiation with the beryllium cap on.

**Figure 9.** PXRD plots of complex 3 as a function of temperature (Cobalt radiation with the beryllium cap on).

**Figure 10.** Variable temperature PXRD of the complex 4 using Cobalt radiation.

**Figure 11.** PXRD (Cobalt radiation with the beryllium cap on) plots of complex 2 as function of pressure.

**Figure 12.** PXRD patterns of complex 3 at high temperature and pressure (Cobalt radiation with the beryllium cap on).

**Figure 13.** PXRD (Cobalt radiation with the beryllium cap on) plots of complex 4 as function of pressure.

**Figure 14.** CO₂ uptake in complex 2 at high pressure and room temperature.

**Experimental Procedure:**

Tetrahedral organic linker, 1 was successfully synthesized using the reported procedure.¹

**Complex 2:** Equi-molar ratio of 1 (61.6 mg, 0.1mmol) and Zn(NO₃)₂·6H₂O (29.7 mg, 0.1 mmol, Aldrich) were dissolved in 10ml DMF in a 20 ml vial. The reaction mixture was ultrasonicated until homogeneous (approx. for 1 min). The reaction vial was capped tightly and placed in an oven at 103 °C. After 24 hours, the sample was removed from the oven and allowed to cool to RT. The mother liquor was decanted to get the transparent crystals, which were washed with DMF (3 mL × 3) and dried in air for 10 min.

**Complex 3** (with Pyrazine): Equi-molar ratio of 1 (61.6 mg, 0.1mmol), Zn(NO₃)₂·6H₂O (29.7 mg, 0.1 mmol, Aldrich) and Pyrazine (8.0 mg, 0.1 mmol) were dissolved in 10ml DMF in a 20 ml vial. The reaction mixture was ultrasonicated until homogeneous (approx. for 1 min). The reaction vial was capped tightly and placed in an oven at 103 °C. After 24 hours, the sample was removed from the oven and allowed to cool to RT. The mother liquor was decanted to get the transparent crystals, which were washed with DMF (3 mL × 3) and dried in air for 10 min.

**Complex 3** (without Pyrazine): Equi-molar ratio of 1(61.6 mg, 0.1mmol), Zn(NO₃)₂·6H₂O (29.7 mg, 0.1 mmol, Aldrich) were dissolved in 10ml DMF in a 23 ml Teflon autoclave and the reaction mixture was ultrasonicated until homogeneous (approx. for 1 min). Then the autoclave heated in oven at 110 °C for 24h and cooled to RT slowly. The crystals were washed with DMF (3 mL × 3) and air dried to get 3.

**Complex 4** (with DABCO): Equi-molar ratio of 1 (61.6 mg, 0.1mmol), Zn(NO₃)₂·6H₂O (29.7 mg, 0.1 mmol, Aldrich) and Diazabicyclo[2,2,2]octane (11.2 mg, 0.1 mmmol) were dissolved in 10ml DMF in a 23 ml Teflon lined autoclave. The reaction mixture was ultrasonicated for a minute to get homogenous. Then the autoclave heated at 110 °C for 24h and then gradually cooled to RT at the rate of 10 °C/hr. The crystals were washed with DMF and air dried.
**Figure 1.** Coordination environment around the metal before and after solvent removal from 2-4.

**Figure 2.** Three fold interpenetrated PtS network generated from tetrahedral organic linker 1 and Zn$_2$ paddle-wheel clusters.
Figure 3. Two interpenetrated Adamantanoid network generated with trapped solvent molecules.

Figure 4. Two-fold interpenetrated Lonsdaleite network generated from tetrahedral building block, 1 and Zn2 clusters.

Figure 5. Thermogravimetric analysis of complex 2 between room temperature and 250 C. Notice the 17% of weight loss.
Figure 6. Thermal analysis of complex 3 with a heating rate of 5 deg/min.

Figure 7. Thermogravimetric analysis of complex 4.

Figure 8. Variable temperature PXRD of the complex 2 using Cobalt radiation with the beryllium cap on.
Figure 9. PXRD plots of complex 3 as a function of temperature (Cobalt radiation with the beryllium cap on).

Figure 10. No change in PXRD (Cobalt radiation with the beryllium cap on) plots of complex 4 at variable temperatures indicating the porous nature of the sample.

Figure 11. PXRD (Cobalt radiation with the beryllium cap on) plots of complex 2 as function of pressure.
Figure 12. PXRD patterns of complex 3 at high temperature and pressure (Cobalt radiation with the beryllium cap on).

Figure 13. PXRD (Cobalt radiation with the beryllium cap on) plots of complex 4 as function of pressure.

Figure 14. CO₂ uptake in complex 2 at high pressure and room temperature.

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