

Electronic Supplementary Information

Supramolecular approaches to metal-organic gels using 'Chevrel-type' coordination clusters as building units

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Experimental Section

Materials and Instrumentation. Commercially available reagents were bought from Sigma-Aldrich and used as received without further purification. Fourier transform infrared spectroscopy (FTIR) data were collected on a PerkinElmer Spectrum 100 FT-IR Spectrometer. Elemental analyses (C, H, and N) were obtained from Microanalysis Lab, School of Chemistry & Chemical Biology, University College Dublin. Electrospray Ionization (ESI) mass spectra were collected using a TOF-MS (Time-of-Flight-Mass Spectrometry, LCT Premier) instrument supplied by Waters Corp. The morphologies of the gels were characterized by a Carl Zeiss Ultra SEM and an FEI Titan TEM. The compositions of gels were studied with an Oxford X-max energy dispersive spectrometer (EDS) equipped on the Carl Zeiss Ultra SEM.

Synthesis of $[\text{Cl-Mn}^{\text{III}}_6(\text{tert-butyl-PO}_3)_8(4\text{-picoline})_6]\text{Cl}\cdot\text{H}_2\text{O}$ ([1]** $\text{Cl}\cdot\text{H}_2\text{O}$):** A mixture of $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ (0.198 g, 1.0 mmol), KMnO_4 (0.032 g, 0.2 mmol), *tert*-butylphosphonate acid (0.136 g, 1.0 mmol), 1,4-phenylenediacetic acid (0.193 g, 1.0 mmol), 4-picolin (0.24 ml) and CH_3CN (25 ml) was stirred at room temperature for 5 h. The resultant solution was filtered and the filtrate was kept at room temperature. Brown crystals of **[1]** $\text{Cl}\cdot\text{H}_2\text{O}$ were obtained within several weeks. Yield: 58% (based on Mn). CHN analysis on dried sample expected for **[1]** $\text{Cl}\cdot 3\text{H}_2\text{O}$ ($\text{Mn}_6\text{P}_8\text{O}_{27}\text{N}_6\text{C}_{68}\text{H}_{120}\text{Cl}_2$): calcd. (found) C 38.85 (37.74), H 5.75 (5.36), N 4.00 (3.90)%.

Synthesis of $[\text{Cl-Mn}^{\text{III}}_6(\text{tert-butyl-PO}_3)_8(\text{pyridine})_6][\text{Mn}^{\text{III}}(\text{Cl})_4]\cdot 1.5\text{H}_2\text{O}$ ([2]** $[\text{Mn}^{\text{III}}(\text{Cl})_4]\cdot 5\text{H}_2\text{O}$):** Similar synthetic procedure as for **[1]** $\text{Cl}\cdot\text{H}_2\text{O}$, except that pyridine (0.24 ml) was used instead of 4-picolin. Brown crystals of **[2]** $[\text{Mn}^{\text{III}}(\text{Cl})_4]\cdot 5\text{H}_2\text{O}$ were obtained within several weeks. Yield: 51% (based on Mn). CHN analysis on dried sample expected for **[2]** $[\text{Mn}^{\text{III}}(\text{Cl})_4]\cdot 1.5\text{H}_2\text{O}$ ($\text{Mn}_7\text{P}_8\text{O}_{25.5}\text{N}_6\text{C}_{62}\text{H}_{105}\text{Cl}_5$): calcd. (found) C 34.60 (34.17), H 4.92 (4.60), N 3.90 (4.08)%.

Synthesis of $[\text{Cl-Mn}^{\text{III}}_6(\text{tert-butyl-PO}_3)_8(\text{MeOH})_4(\text{H}_2\text{O})_2]\text{Cl}\cdot 2\text{H}_2\text{O}$ ([3]Cl·2H₂O): A mixture of $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ (0.195 g, 1.0 mmol), KMnO_4 (0.031 g, 0.2 mmol), *tert*-butylphosphonate acid (0.136 g, 1.0 mmol), 4,4'-dipyridine (0.078 g, 0.5 mmol) and CH_3OH (30 ml) was stirred at room temperature for 5 h. The resultant solution was filtered and the filtrate was kept at room temperature. Red crystals of [3]Cl·2H₂O were obtained within several weeks. Yield: 66% (based on Mn).

Synthesis of $[\text{Cl-Mn}^{\text{III}}_6(\text{tert-butyl-PO}_3)_8(4\text{-pyridinecarboxaldehyde})_4(\text{H}_2\text{O})_2]\text{Cl}$ ([4]Cl): A mixture of $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ (0.098 g, 0.5 mmol), KMnO_4 (0.016 g, 0.1 mmol), *tert*-butylphosphonate acid (0.070 g, 0.5 mmol), 4-pyridinecarboxaldehyde (0.065 ml) and CH_3CN (20 ml) was stirred at room temperature for 5 h. The resultant solution was filtered and the filtrate was kept at room temperature. Red crystals of [4]Cl were obtained within several weeks. Yield: 46% (based on Mn).

Synthesis of $[\text{Cl-Mn}^{\text{III}}_6(\text{tert-butyl-PO}_3)_8(\text{pyridine})_4(4,4'\text{-dipyridine})]\text{Cl}$ ([5]Cl): A mixture of $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ (0.100 g, 0.5 mmol), KMnO_4 (0.016 g, 0.1 mmol), *tert*-butylphosphonate acid (0.069 g, 0.5 mmol), pyridine (0.06 ml) and CH_3CN (10 ml) was stirred at room temperature for 2 h. Then 4,4'-dipyridine (0.080 g, 0.5 mmol) and NH_4BF_4 (0.213 g, 2.0 mmol) were added to the solution. The resultant reaction mixture was transferred to a 23 ml Teflon liner and sealed in a Parr autoclave. The autoclave was then heated at 120 °C for 5 days. After cooled to room temperature, a few red, needle crystals of [5]Cl were found together with lots of yellow precipitates. Yield: 12% (based on Mn).

Preparation of metal-organic gels (MOGs) 6: A mixture of $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ (0.098 g, 0.5 mmol), KMnO_4 (0.019 g, 0.1 mmol), *tert*-butylphosphonate acid (0.071 g, 0.5 mmol), 1,4-phenylenediacetic acid (0.099 g, 0.5 mmol), 4,4'-dipyridine (0.156 g, 1.0 mmol), Et_3N (0.13 ml) and CH_3CN (20 ml) was stirred at room temperature for 5 h. The resultant solution was filtered and the filtrate was kept at room temperature. Brown gels formed within one week. CHN analysis on dried sample expected for

$[\text{Cl} \leftarrow \text{Mn}_6(\text{tert-butyl-PO}_3)_8(4,4'\text{-dipyridine})_6](\text{Cl}) \cdot 5\text{H}_2\text{O}$ ($\text{Mn}_6\text{P}_8\text{O}_{29}\text{N}_{12}\text{C}_{92}\text{H}_{130}\text{Cl}_2$): calcd.
(found) C 43.91 (45.14), H 5.21 (6.13), N 6.68 (6.68)%.

Preparation of SEM samples:

(A) A small quantity of the gel **6** was put onto the top of a silicon surface, and then dried at 80 °C for 24 hours.

(B) Gels were agitated to form a liquid phase. One drop of this liquid was deposited on a silicon surface, and dried in air.

(C) A small quantity of the gel **6** were added into a 10 ml methanol solution to form a suspension. Then one drop of this suspension was put onto the top of a silicon surface, and dried in air.

Prior to examination, all the sample were coated with a thin layer of gold, except the one used for EDS analysis.

Preparation of TEM samples: One drop of the suspension of the dried gel of **6** in ethanol was drop-cast onto a carbon-coated copper grid. The TEM grid was dried at room temperature and then subjected to observation.

Magnetic susceptibility measurements: Measurements were performed using a Quantum Design MPMS-XL SQUID magnetometer housed at the Centre de Recherche Paul Pascal in Pessac, France. The measurements were performed on freshly prepared polycrystalline samples covered by a minimum of their frozen mother liquor within a sealed straw to prevent desolvation/degradation of the solid during the measurements. No evaporation of the mother liquor was observed during the measurements. The mass of the sample (12.17 and 8.15 mg for **[1]**Cl·H₂O and **[2]**[Mn^{III}(Cl)₄]·1.5H₂O, respectively) was determined after the measurements and subsequent mother liquor evaporation. dc measurements were conducted from 270 to 1.8 K at 1000 Oe. A *M* vs *H* measurement was performed at 100 K to confirm the absence of ferromagnetic impurities. The ac susceptibility experiments were performed at various frequencies ranging from 1 to 1500 Hz with an ac field amplitude of 3 Oe in zero dc field. It is worth noting that no significant out-of-phase ac susceptibility signal has been

detected above 1.8 K for these compounds. Experimental data were corrected for the sample holder and for the diamagnetic contributions of the sample and mother liquor.

X-ray Crystallography. Single crystal X-ray structure determination of the five compounds, **[1]**Cl·H₂O, **[2]**[Mn^{III}(Cl)₄]·5H₂O, **[3]**Cl·2H₂O, **[4]**Cl and **[5]**Cl was performed at 150(K) on the Bruker SMART Apex diffractometer using graphite-monochromated Mo-K α radiation. Absorption corrections were applied using SADABS.¹ Structures were solved by direct method and refined by full-matrix least-squares on F² using *SHELXTL*.²

For **[1]**Cl·H₂O, SIMU and DELU restraints were used to improve the data to parameter ratio and to make the atomic displacement parameters more reasonable. SIMU restrains the anisotropic displacement parameters of adjacent atoms to be similar, and DELU enforces that the main directions of movement of covalently bonded atoms are the same. For **[2]**[Mn^{III}(Cl)₄]·5H₂O, contributions to scattering due to disordered solvent molecules were removed using the *SQUEEZE* routine of *PLATON*,³ the contribution of disordered solvent molecules removed by the *SQUEEZE* routine was then included in the overall formula, formula weight, density, F(000), etc. and the structure was then refined again using the data generated. The occupancies of partial-occupancy atoms were determined considering thermal displacement parameters, charge considerations of cationic clusters and CHN analyses. For **[4]**Cl, DFIX restraints were used to restrain the H–O distances and H–O–H angles. For **[2]**[Mn^{III}(Cl)₄]·5H₂O and **[5]**Cl, ISOR restraints were used to restrain the anisotropic displacement parameters. Crystal data and details of data collection and refinement were summarized in Table S1.

Crystallographic data, CCDC 886125–886127, 886524 and 886525 can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(1) Sheldrick, G. M. *SADABS, Program for area detector adsorption correction*. Institute for Inorganic Chemistry, University of Göttingen, Göttingen (Germany), **1996**.

(2) Sheldrick, G. M. *SHELXL-97, Program for solution of crystal structures*. University of Göttingen, Göttingen (Germany), **1997**.

(3) Vandersluis, P.; Spek, A. L. *Acta Crystallogr. A* **1990**, *46*, 194.

Table S1. Crystal Data and Structure Refinements for [1]Cl·H₂O, [2][Mn^{III}(Cl)₄·5H₂O, [3]Cl·2H₂O, [4]Cl and [5]Cl.

	[1]Cl·H ₂ O	[2][Mn ^{III} (Cl) ₄ ·5H ₂ O	[3]Cl·2H ₂ O	[4]Cl	[5]Cl
CCDC No	886125	886126	886524	886525	886127
Crystal. determ. formula	C ₆₈ H ₁₁₆ Cl ₂ Mn ₆ N ₆ O ₂₅ P ₈	C ₆₂ H ₁₁₂ Cl ₅ Mn ₇ N ₆ O ₂₉ P ₈	C ₃₆ H ₉₆ Cl ₂ Mn ₆ O ₃₂ P ₈	C ₅₆ H ₉₆ Cl ₂ Mn ₆ N ₄ O ₃₀ P ₈	C ₆₂ H ₁₀₀ Cl ₂ Mn ₆ N ₆ O ₂₄ P ₈
Mr	2066.02	2215.17	1689.43	1953.67	1961.78
crystal system	Cubic	monoclinic	tetragonal	monoclinic	monoclinic
space group	<i>Pa</i> -3	<i>P2</i> ₁ / <i>c</i>	<i>I4</i> / <i>m</i>	<i>C2</i> / <i>c</i>	<i>C2</i> / <i>m</i>
<i>a</i> [Å]	21.244(2)	24.577(5)	14.133(2)	52.51(2)	23.109(5)
<i>b</i> [Å]	21.244(2)	35.726(7)	14.133(2)	15.806(3)	17.421(3)
<i>c</i> [Å]	21.244(2)	14.376(3)	21.552(4)	23.396(5)	14.250(3)
α [°]	90.00	90.00	90.00	90.00	90.00
β [°]	90.00	103.59(3)	90.00	116.45(2)	128.07(3)
γ [°]	90.00	90.00	90.00	90.00	90.00
<i>V</i> [Å ³]	9587.6(16)	12269(4)	4304.8(12)	17385(8)	4516.3(24)
<i>Z</i>	4	4	2	8	2
<i>T</i> [K]	150(2)	150(2)	150(2)	150(2)	150(2)
ρ_c [gcm ⁻³]	1.431	1.199	1.303	1.493	1.443
μ [mm ⁻¹]	1.024	0.967	1.128	1.128	1.082
reflns coll.	2822	21598	1959	15294	4094
unique reflns	2664	14485	1828	9323	3161
GOF	1.077	0.982	1.036	1.040	1.067
<i>R</i> 1 [<i>I</i> >2 σ (<i>I</i>)] ^[a]	0.0934	0.1093	0.0631	0.0747	0.0862
<i>wR</i> 2 [<i>I</i> >2 σ (<i>I</i>)] ^[b]	0.2004	0.3338	0.1816	0.1842	0.2223

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)]\}^{1/2}$.

Table S2. Bond valance sum calculations for clusters **1–5**.

1	Mn site	Mn1					
	BVS	3.384					
	assigned O.S.	+3					
2	Mn site	Mn1	Mn2	Mn3	Mn4	Mn5	Mn6
	BVS	3.195	3.174	3.173	3.185	3.263	3.254
	assigned O.S.	+3	+3	+3	+3	+3	+3
3	Mn site	Mn1	Mn2				
	BVS	3.453	3.395				
	assigned O.S.	+3	+3				
4	Mn site	Mn1	Mn2	Mn3	Mn4	Mn5	Mn6
	BVS	3.201	3.210	3.181	3.185	2.868	2.871
	assigned O.S.	+3	+3	+3	+3	+3	+3
5	Mn site	Mn1	Mn2	Mn3			
	BVS	3.614	3.642	3.667			
	assigned O.S.	+3	+3	+3			

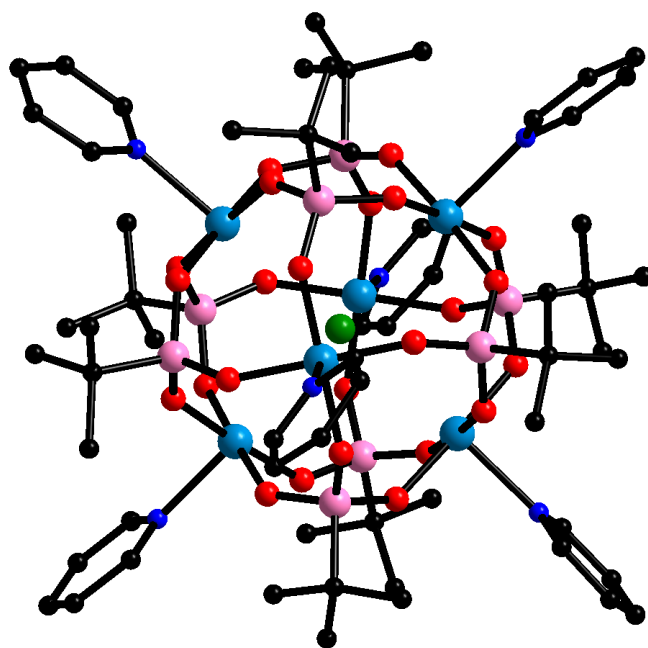


Figure S1. Crystal structure of the hexanuclear complex $[2][\text{Mn}^{\text{III}}(\text{Cl})_4]\cdot 5\text{H}_2\text{O}$. Disordered charge-balancing $[\text{Mn}^{\text{III}}(\text{Cl})_4]$ species and solvents are omitted for clarity.

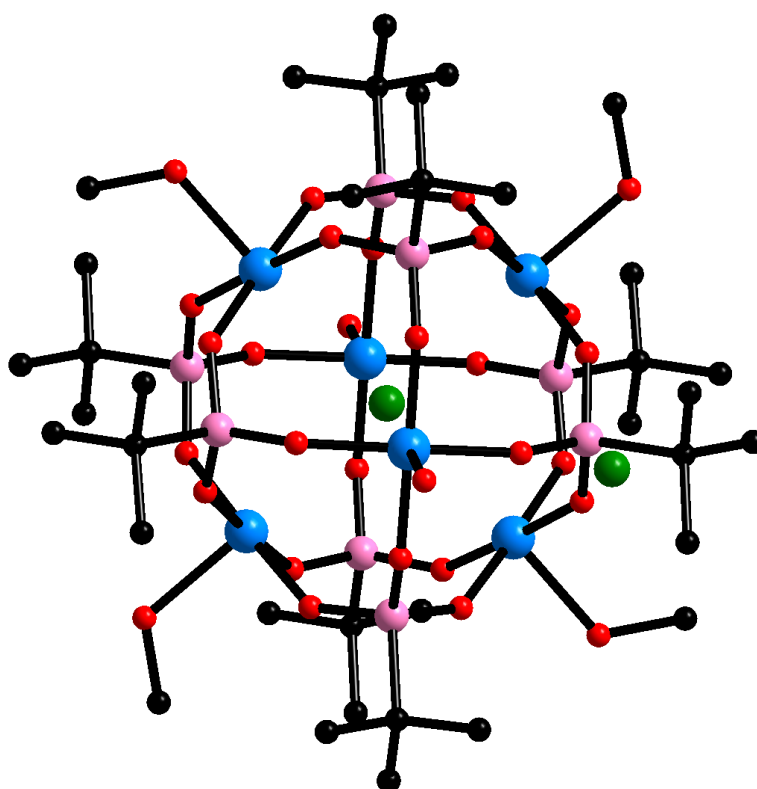


Figure S2. Crystal structure of the hexanuclear complex $[3]\text{Cl}\cdot 2\text{H}_2\text{O}$. The central Cl^- ion locates at the inversion centre and the coordinated water molecule locates at the 4-fold roto-inversion axis. Solvent molecules are omitted for clarity.

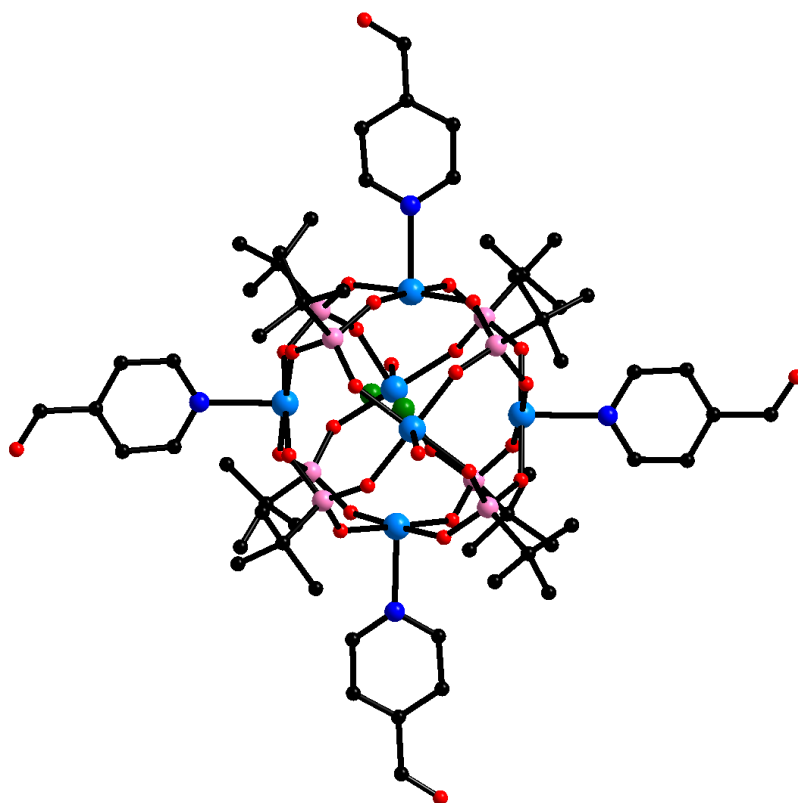


Figure S3. Crystal structure of the hexanuclear complex [4]Cl.

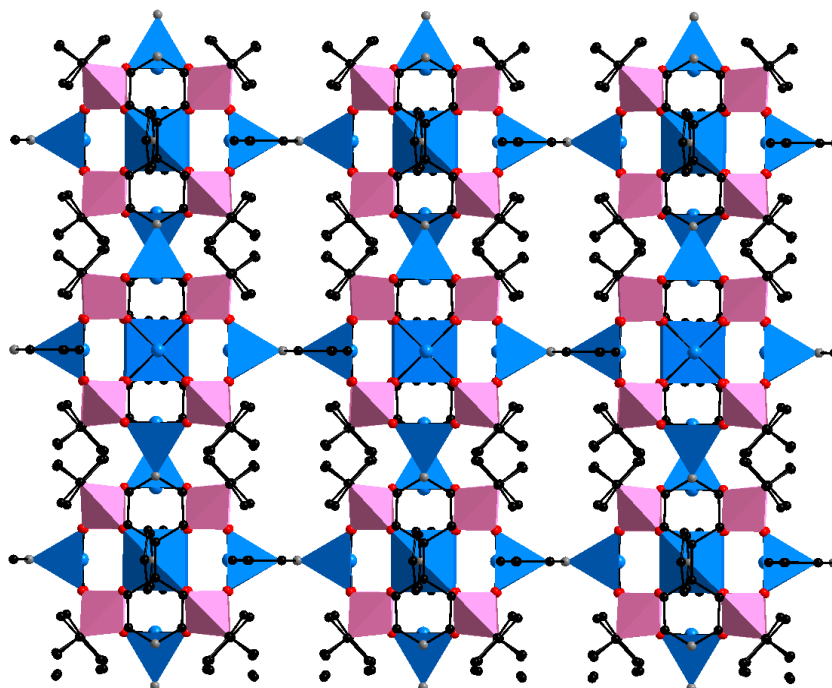


Figure S4. The packing structure of the 1D polymer [5]Cl. View in the direction of the crystallographic *a*-axis. The pyridine ligands locate within the mirror planes. Charge balancing Cl⁻ anion is omitted for clarity.

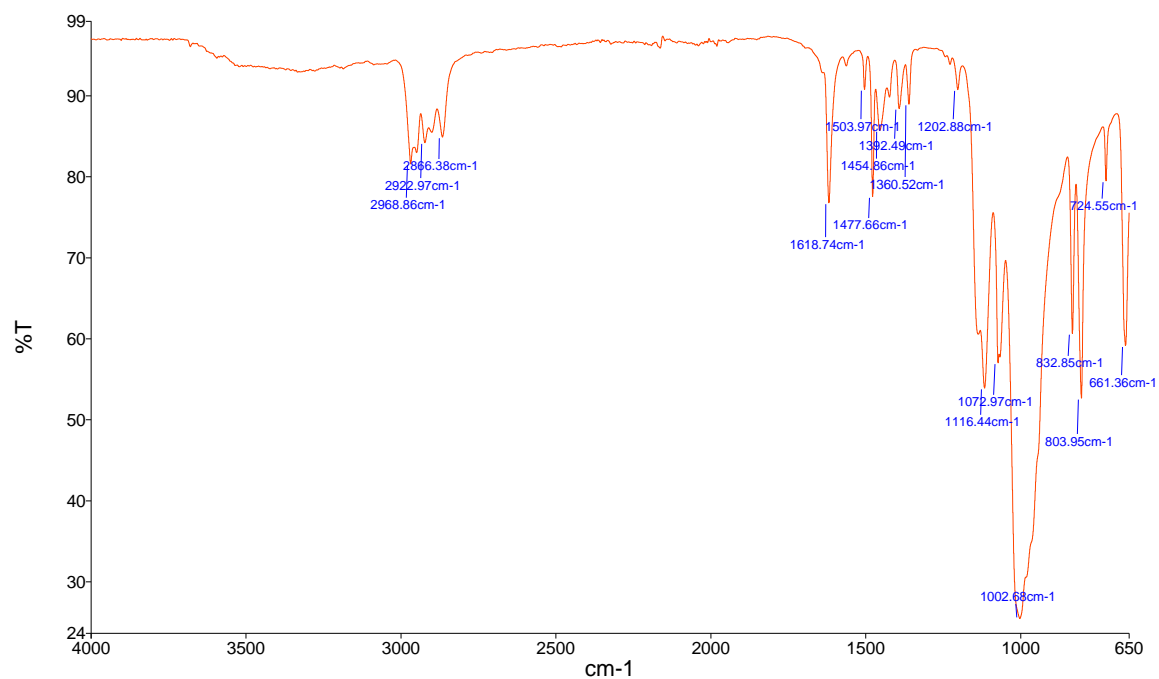


Figure S5. IR spectrum of [1]Cl·H₂O.

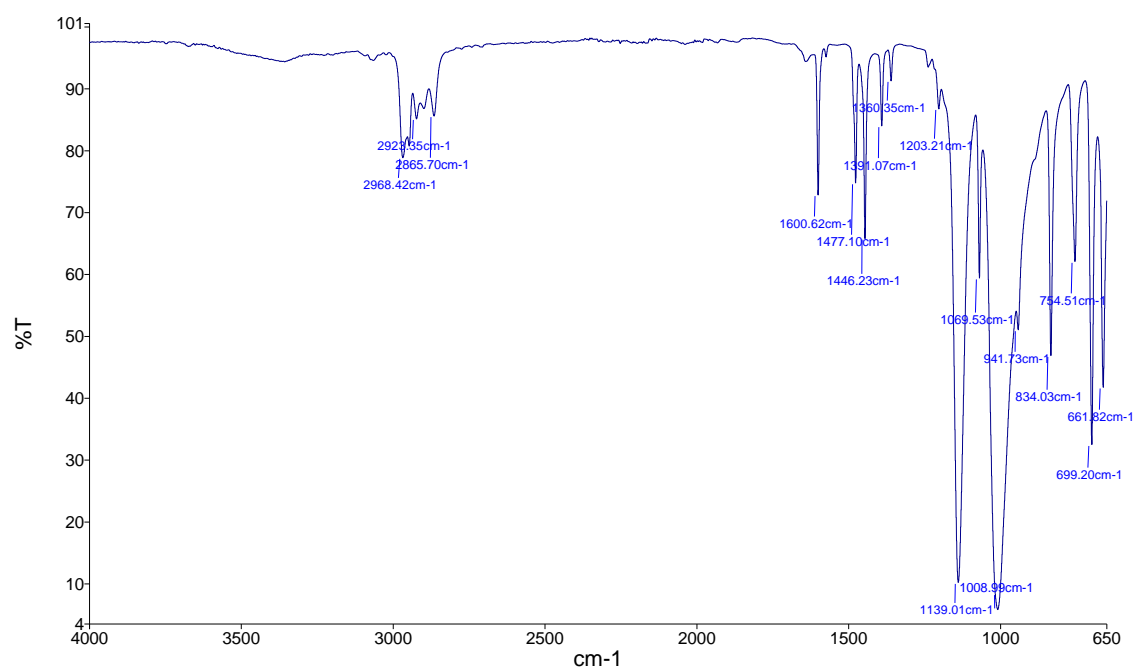


Figure S6. IR spectrum of [2][Mn^{III}(Cl)₄]·5H₂O.

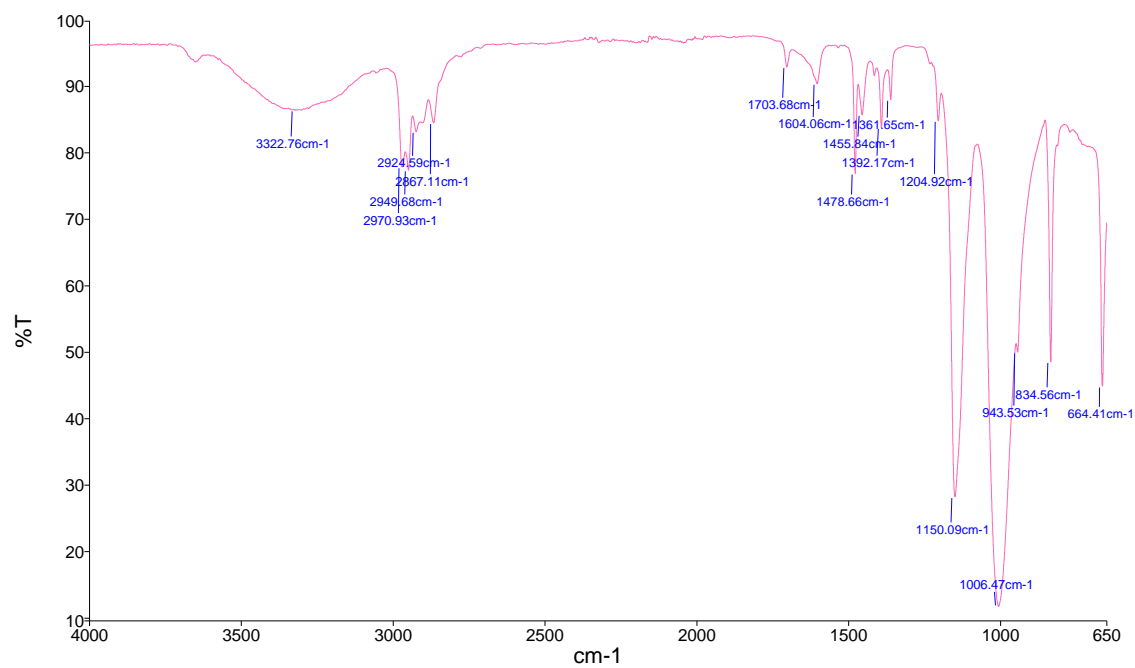


Figure S7. IR spectrum of [3]Cl·2H₂O.

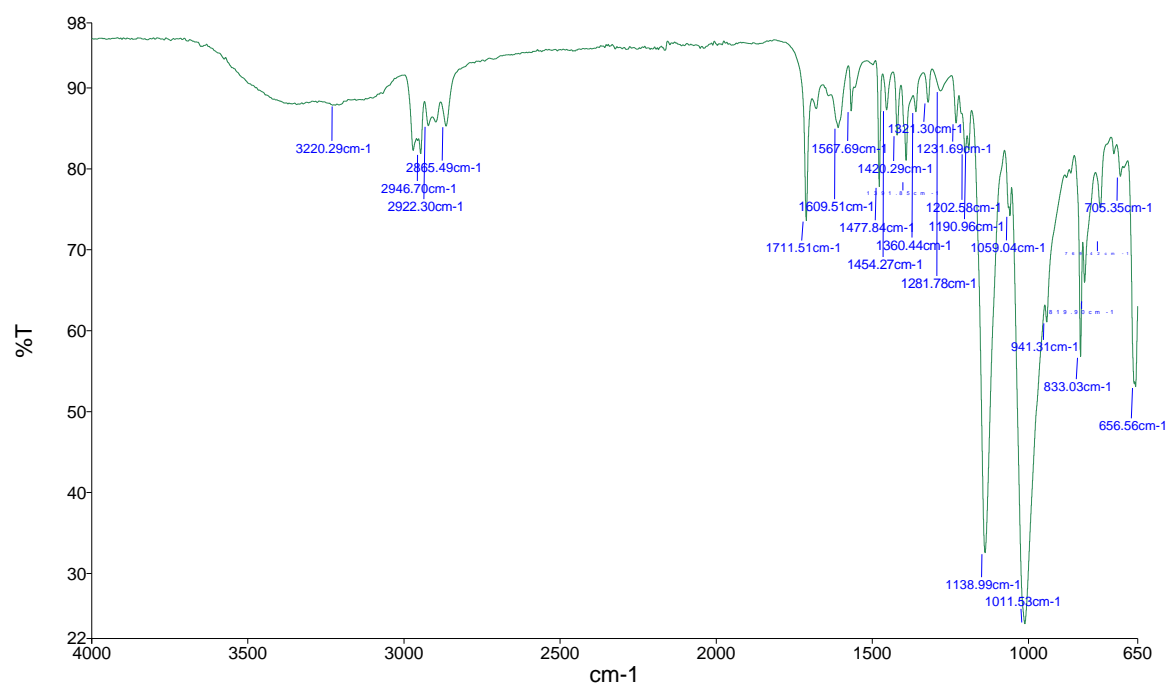


Figure S8. IR spectrum of [4]Cl.

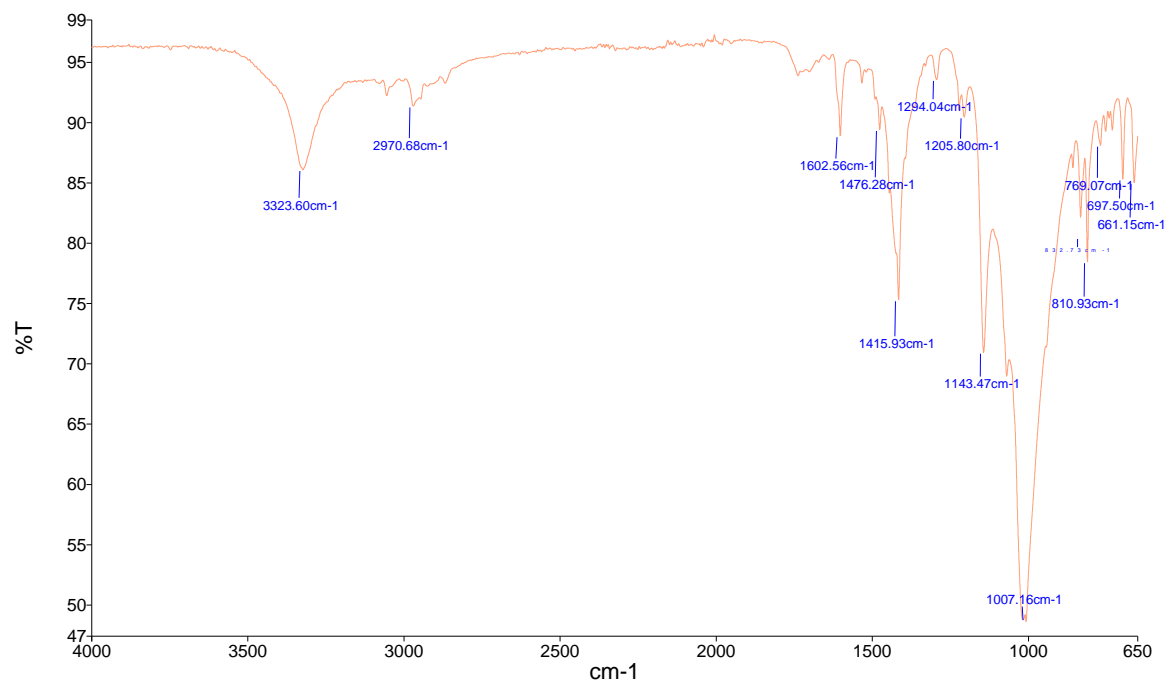


Figure S9. IR spectrum of [5]Cl.

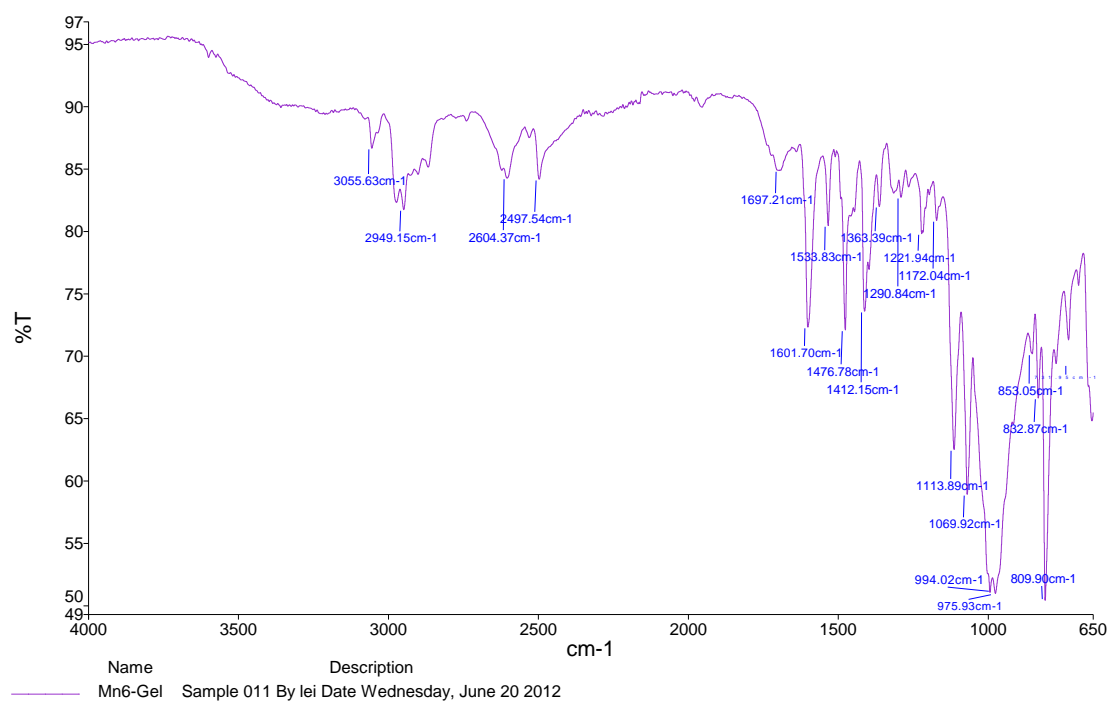


Figure S10. IR spectrum of dried sample of gels 6.

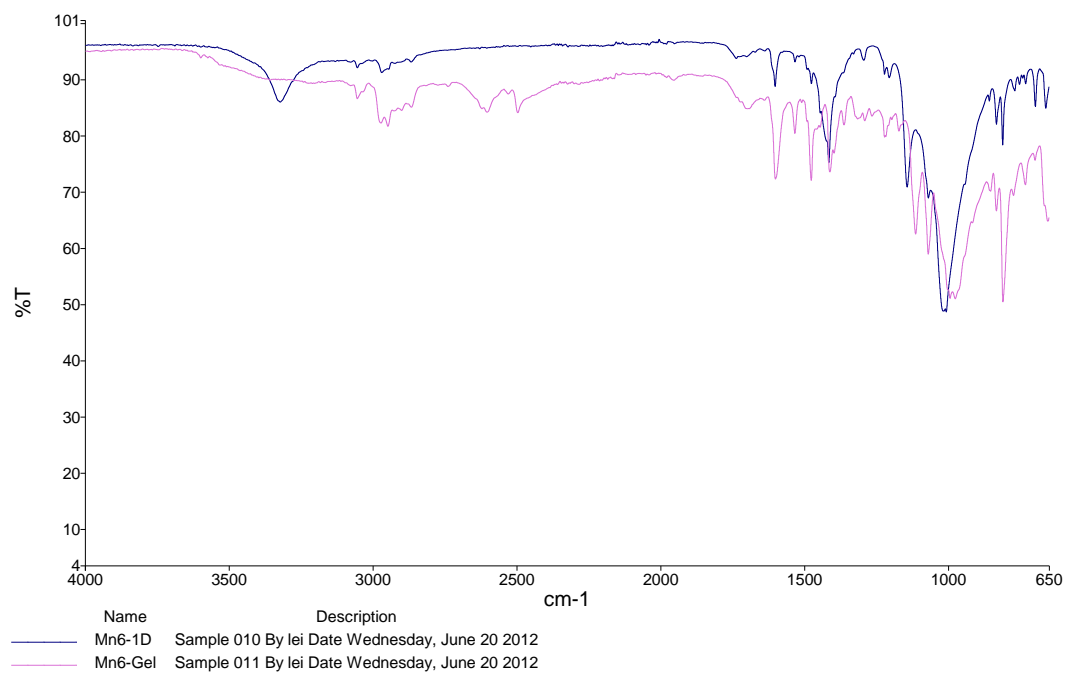


Figure S11. Comparison of the IR spectra of 1D polymer [5]Cl and gel 6.

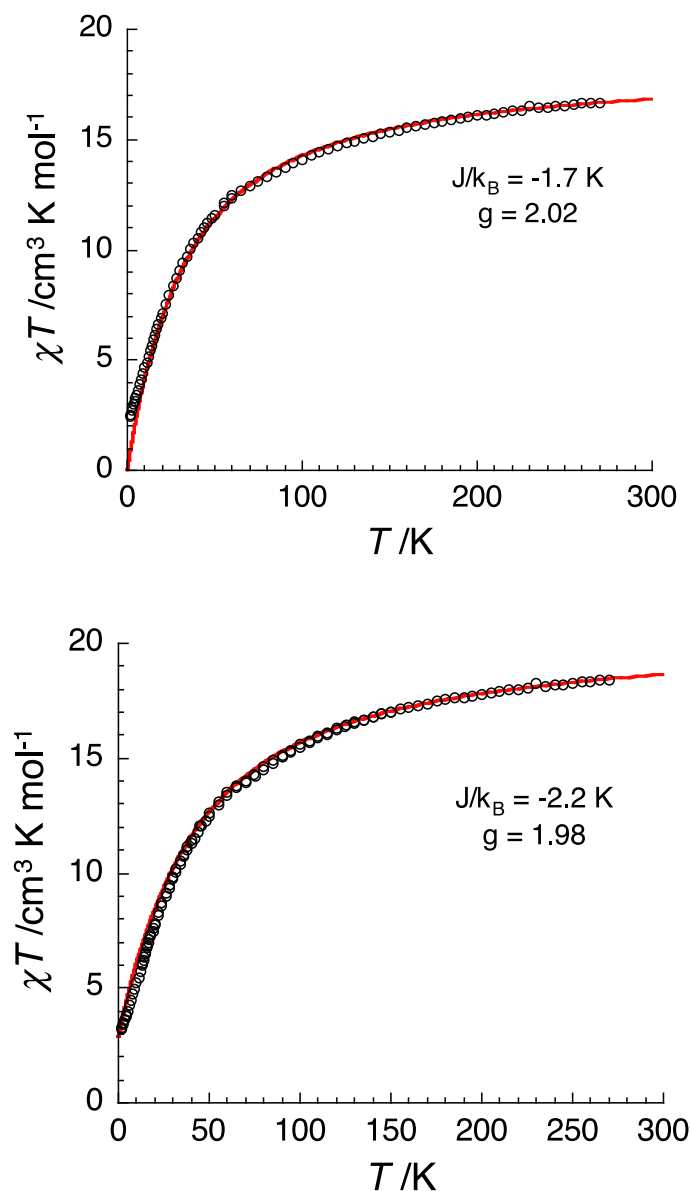


Figure S12. Temperature dependence of the χT product of $[\mathbf{1}]\text{Cl}\cdot\text{H}_2\text{O}$ (top) and $[\mathbf{2}][\text{Mn}^{\text{III}}(\text{Cl})_4]\cdot 1.5\text{H}_2\text{O}$ (bottom) at 1000 Oe (χ is the molar magnetic susceptibility calculated from the ratio of the magnetization over the applied dc magnetic field, M/H , per complex). The solid red lines are the best simulations of the χT vs. T experimental data calculated from the MAGPACK^[1] program with the following isotropic Heisenberg spin Hamiltonian: $\mathbf{H} = -2J ((\mathbf{S}_1 + \mathbf{S}_6)\cdot(\mathbf{S}_2 + \mathbf{S}_3 + \mathbf{S}_4 + \mathbf{S}_5) + \mathbf{S}_2\cdot\mathbf{S}_3 + \mathbf{S}_3\cdot\mathbf{S}_4 + \mathbf{S}_4\cdot\mathbf{S}_5 + \mathbf{S}_2\cdot\mathbf{S}_5)$. [1] (a) J. J. Borrás-Almenar, J. M. Clemente-Juan, E. Coronado and B. S. Tsukerblat, *Inorg. Chem.* 1999, **38**, 6081-6088. (b) J. J. Borrás-Almenar, J. M. Clemente-Juan, E. Coronado and B. S. Tsukerblat, *J. Comput. Chem.* 2001, **22**, 985-991.

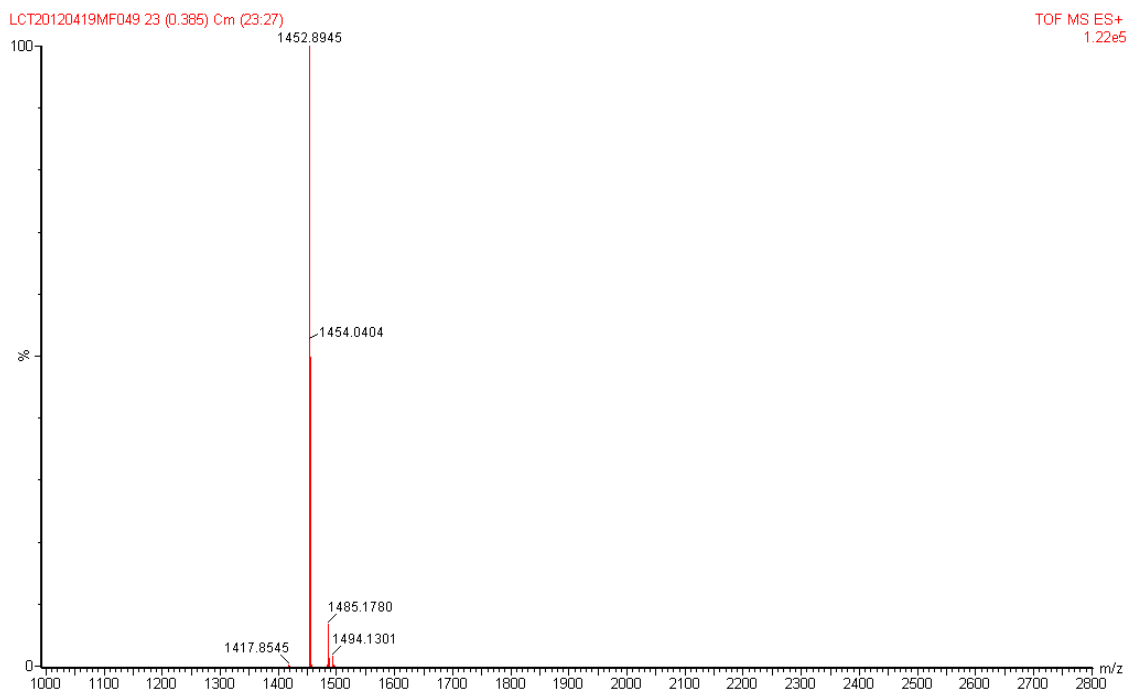


Figure S13. The positive-mode ESI-MS spectrum of [1]Cl·H₂O; samples dissolved in CH₃CN. Signals centered at *m/z* 1452.89 correspond to {Mn₆(*tert*-butyl-PO₃)₈(Cl)}⁺ (calcd. *m/z* 1452.83).

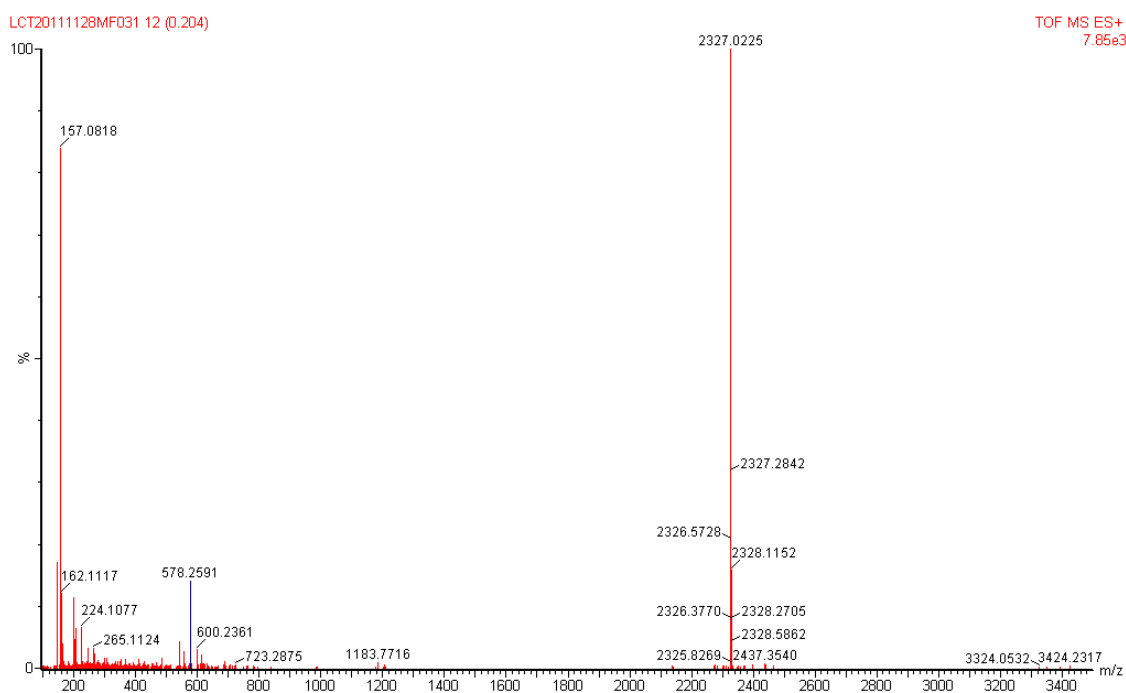
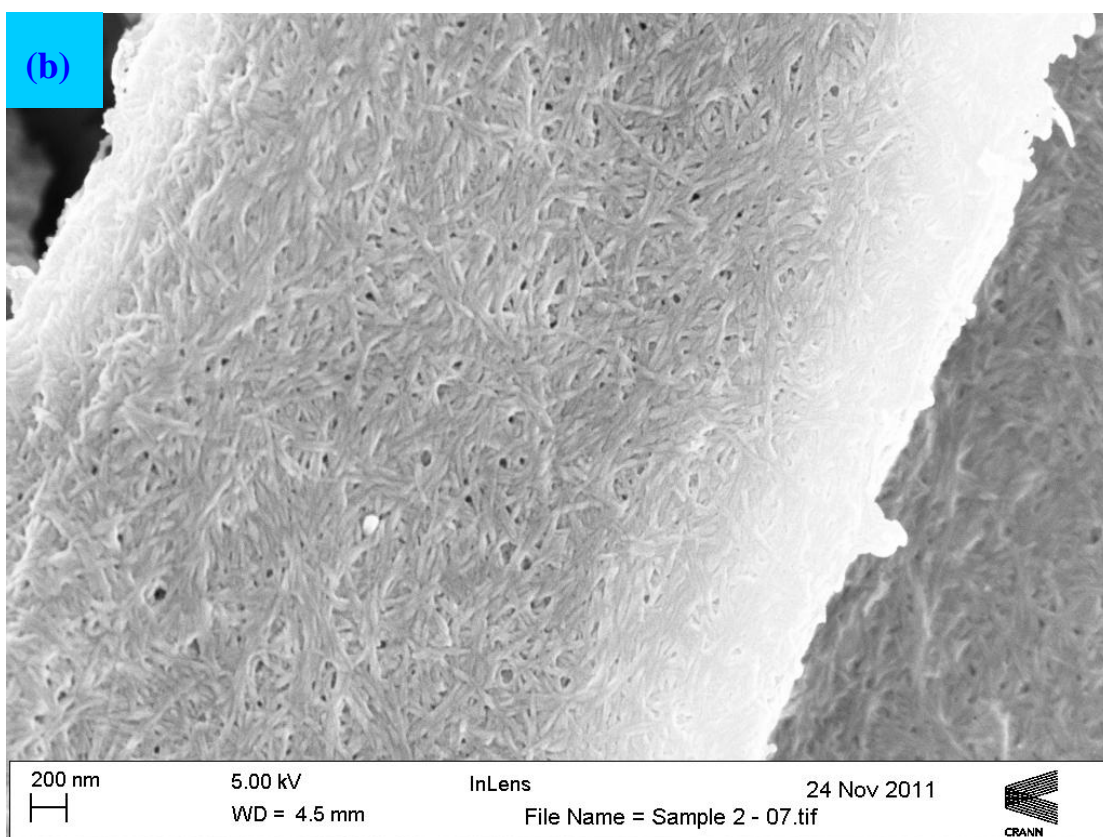
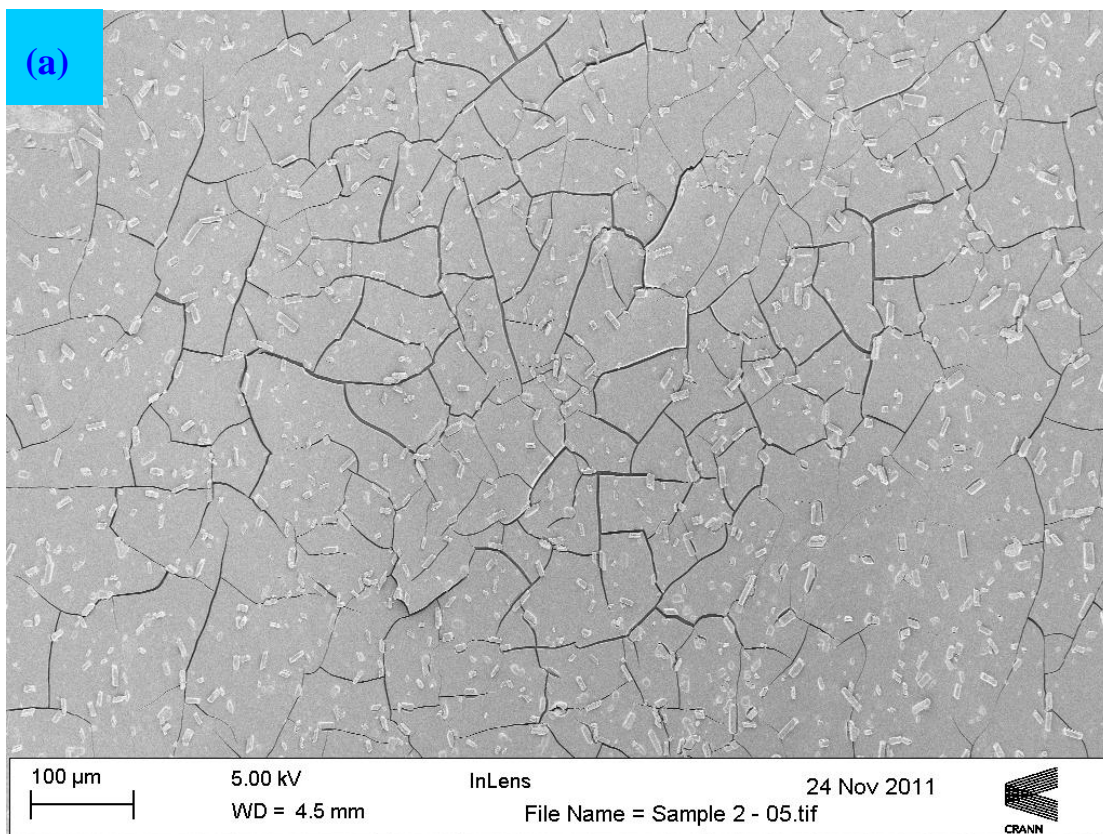
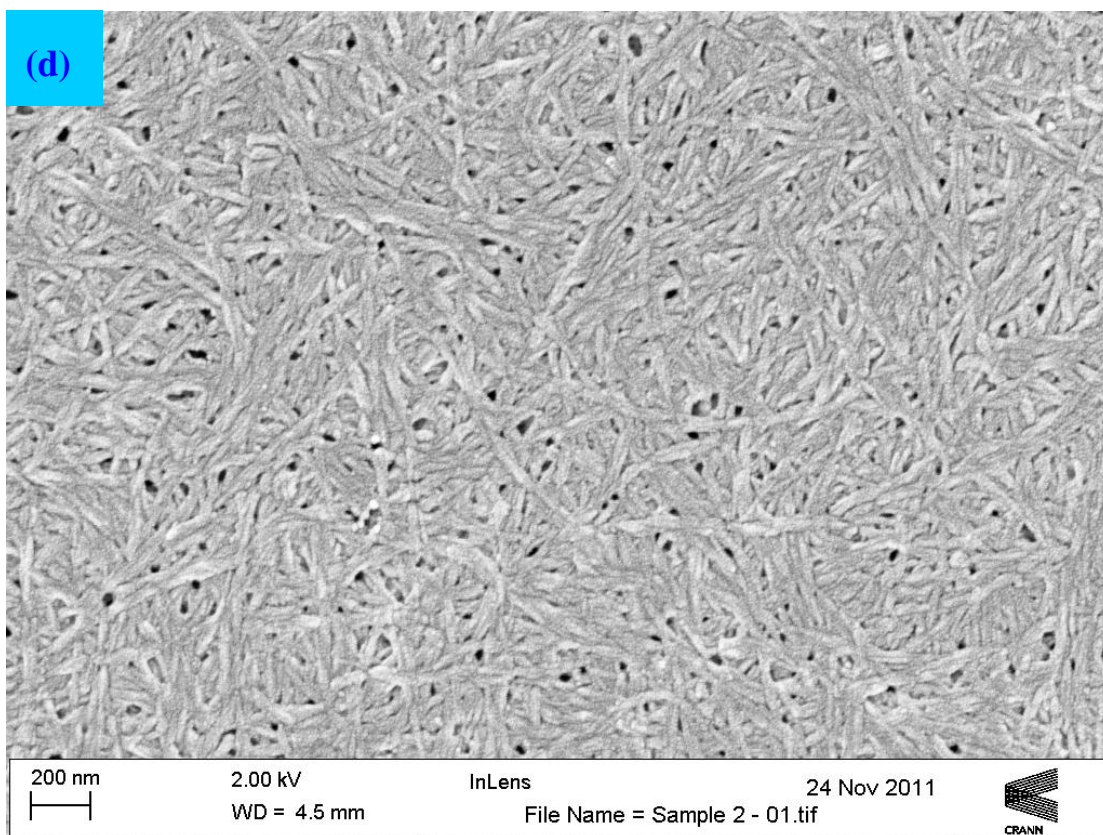
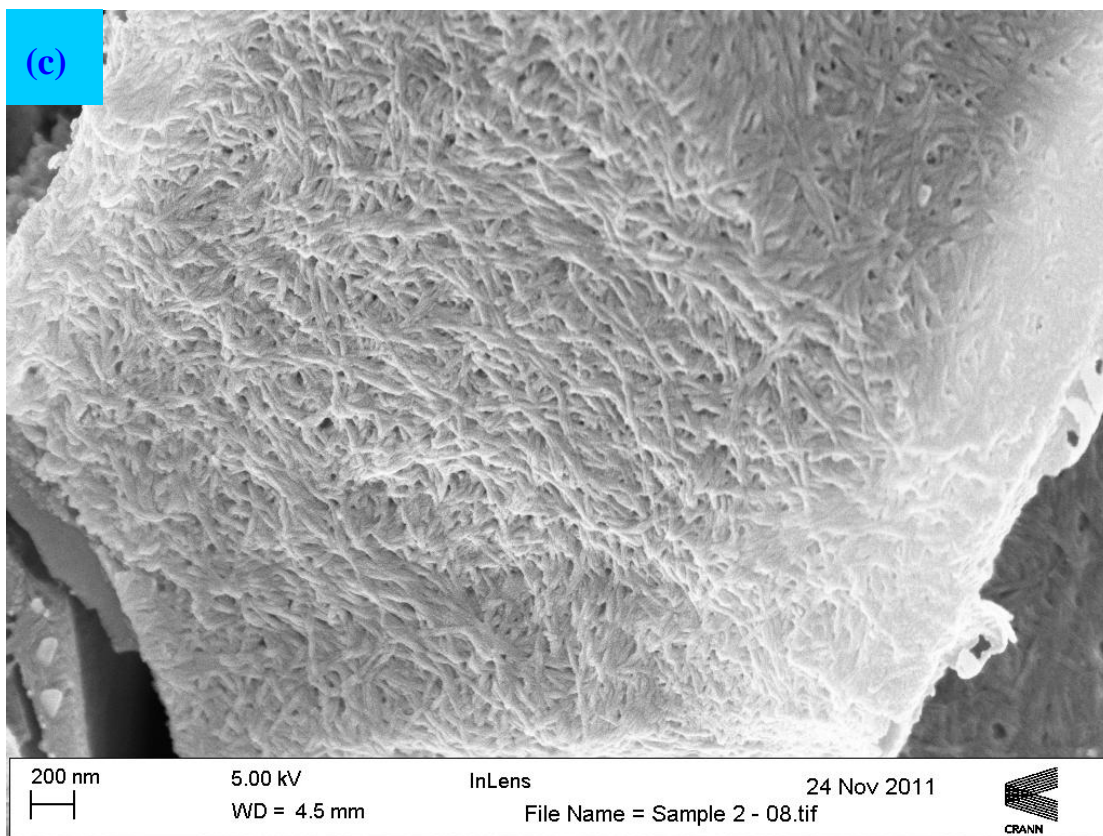


Figure S14. The positive-mode ESI-MS spectrum of the metal-organic gel **6**; samples dissolved in CH₃CN. Signals centered at *m/z* 157.08 and 2327.02 correspond to {4,4'-bipyridine+H}⁺ (calcd. *m/z* 157.08) and {[Mn₆(*tert*-butyl-PO₃)₈(4,4'-dipyridine)₅(Cl)]+(H₃O)₄+H₂O}⁺ (calcd. *m/z* 2327.26), respectively.





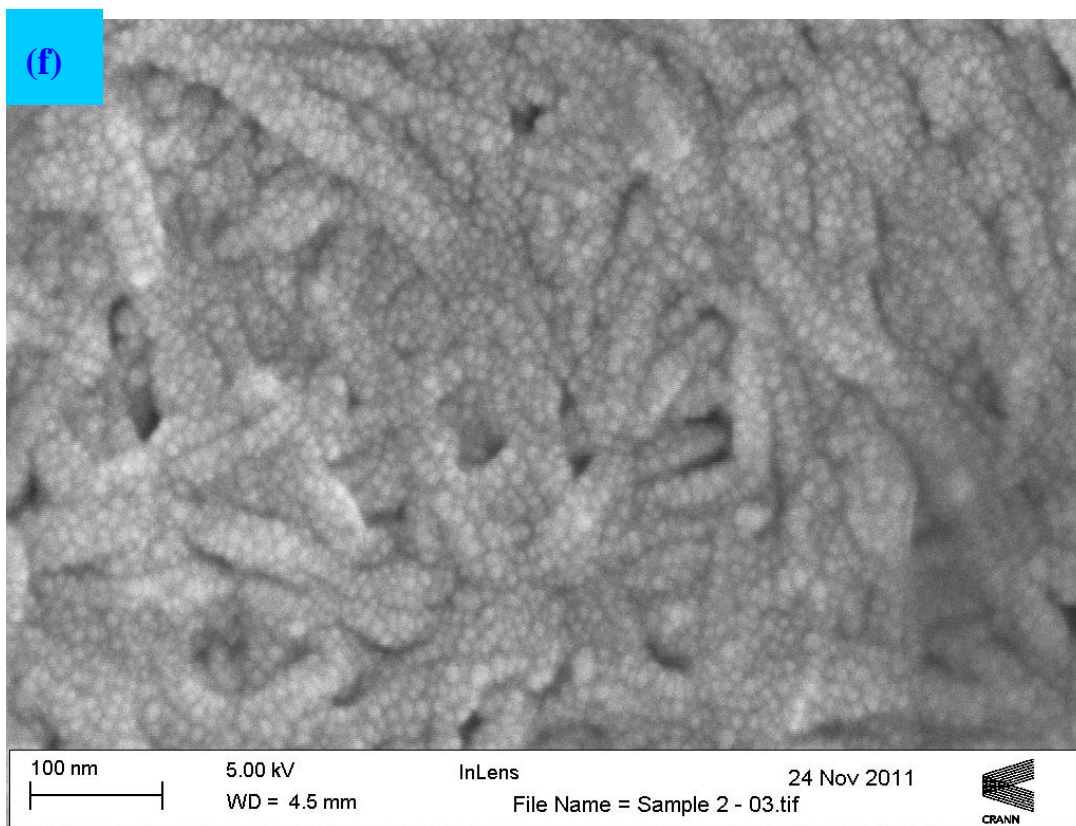
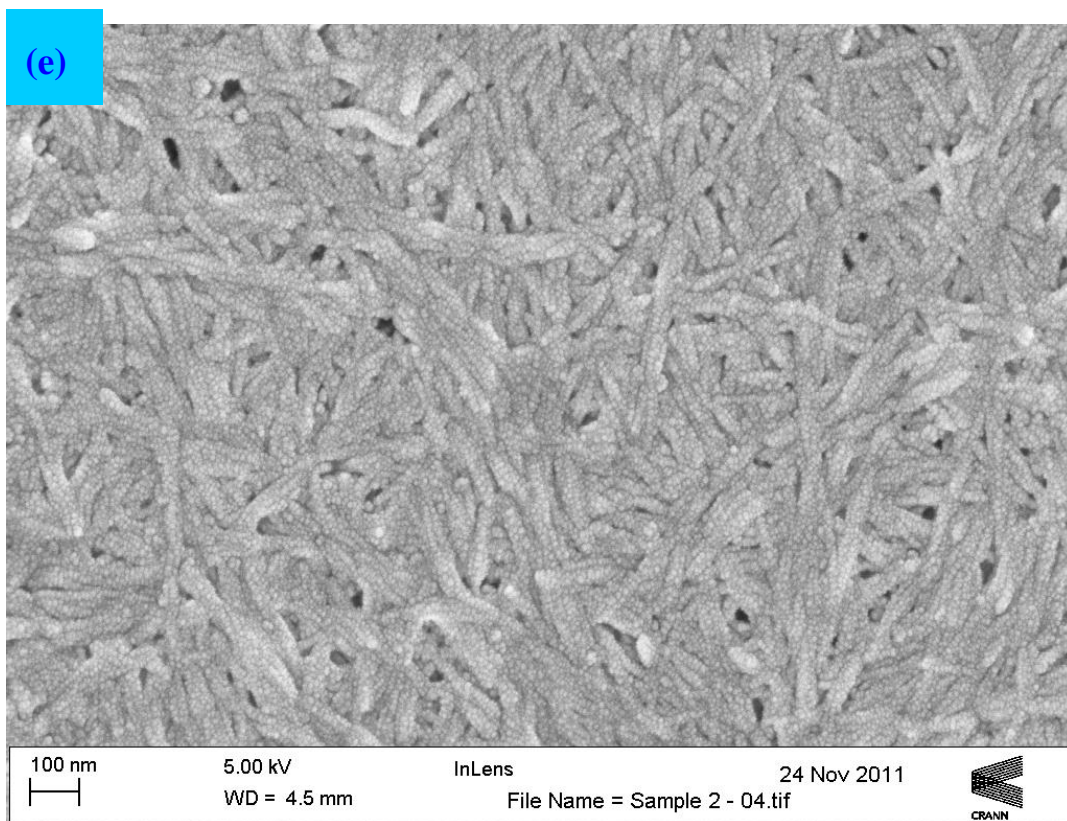
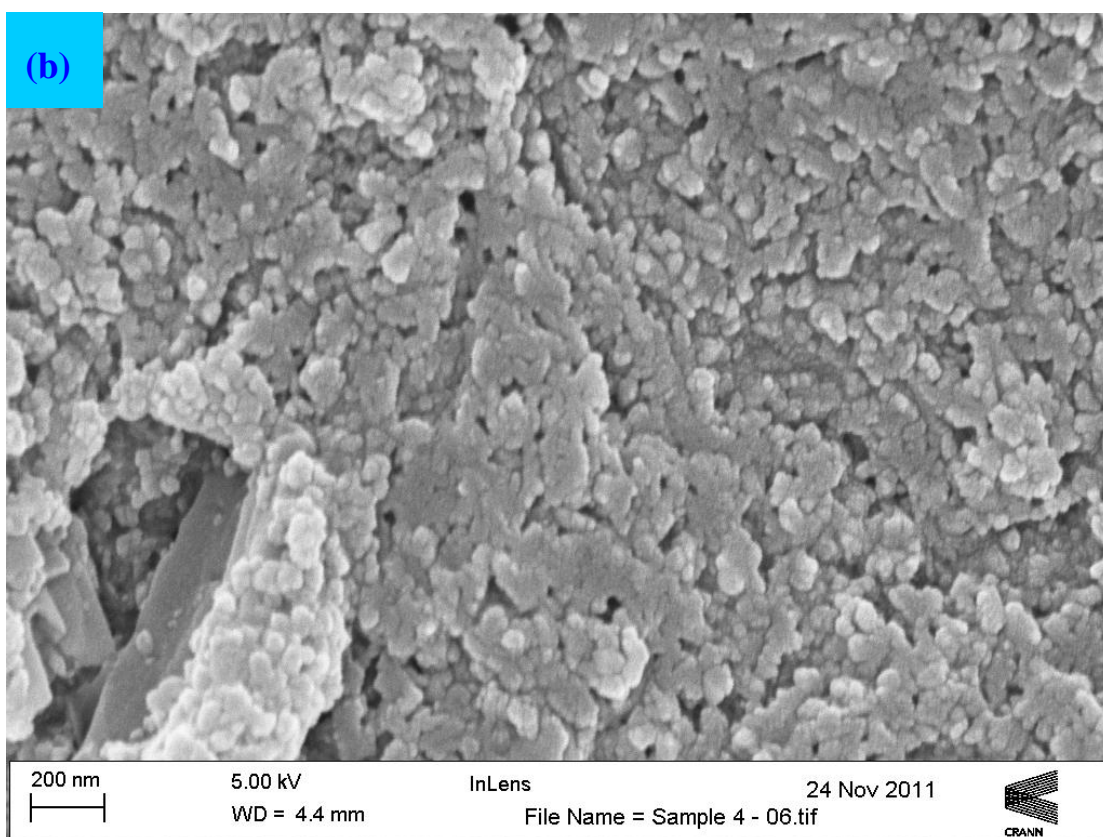
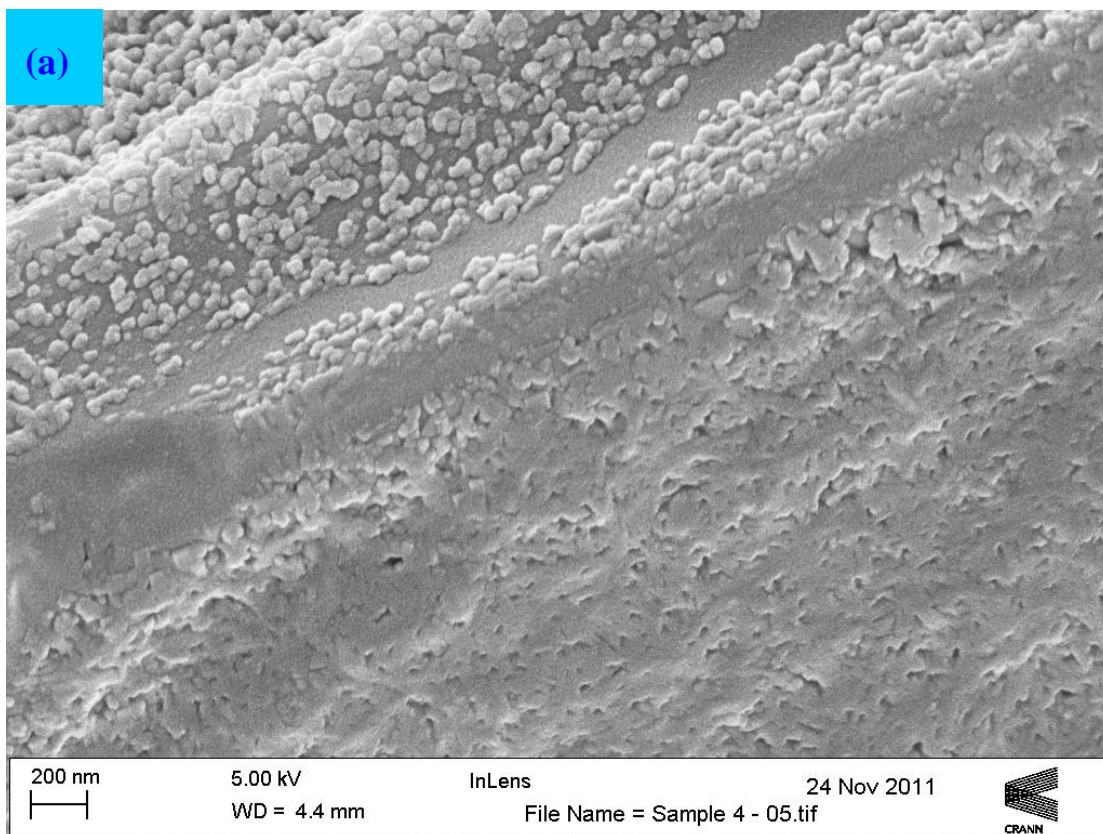


Figure S15. (a)–(f) SEM images of the dried metal-organic gel **6** (SEM sample preparation A).



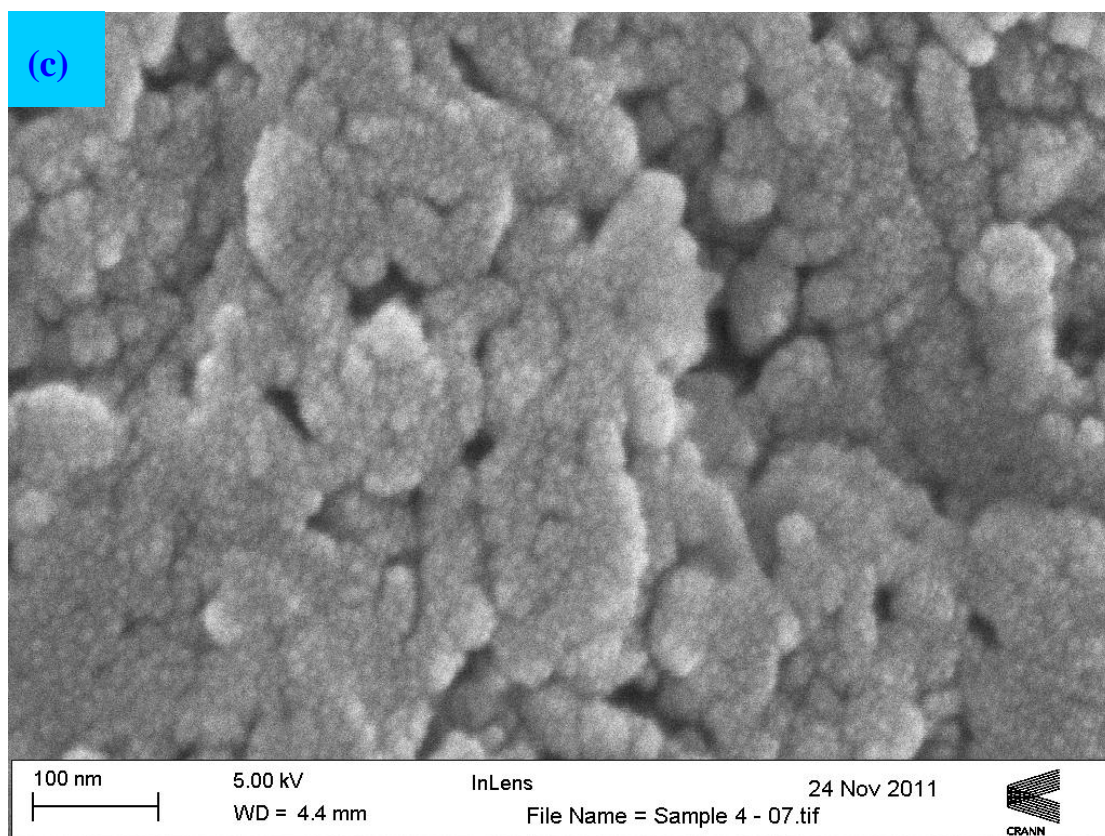


Figure S16. (a)–(c) SEM images of the dried sol phase obtained by shaking metal-organic gel **6** (SEM sample preparation **B**).

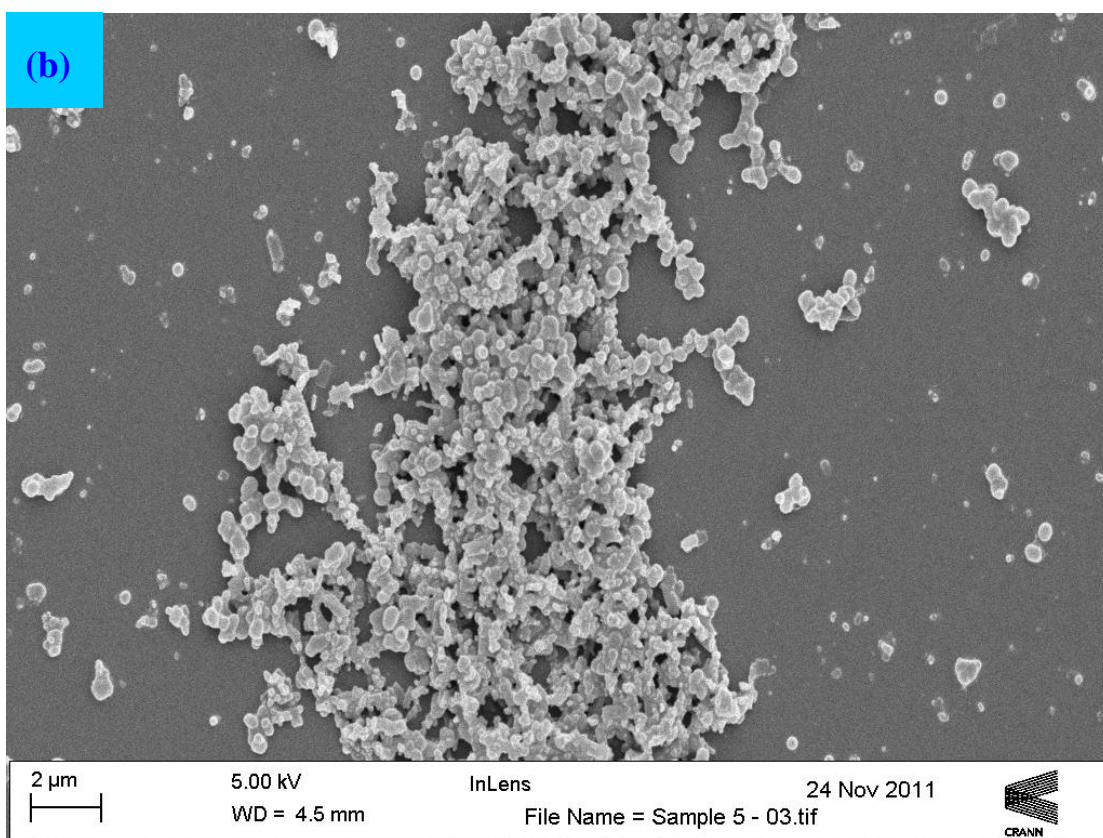
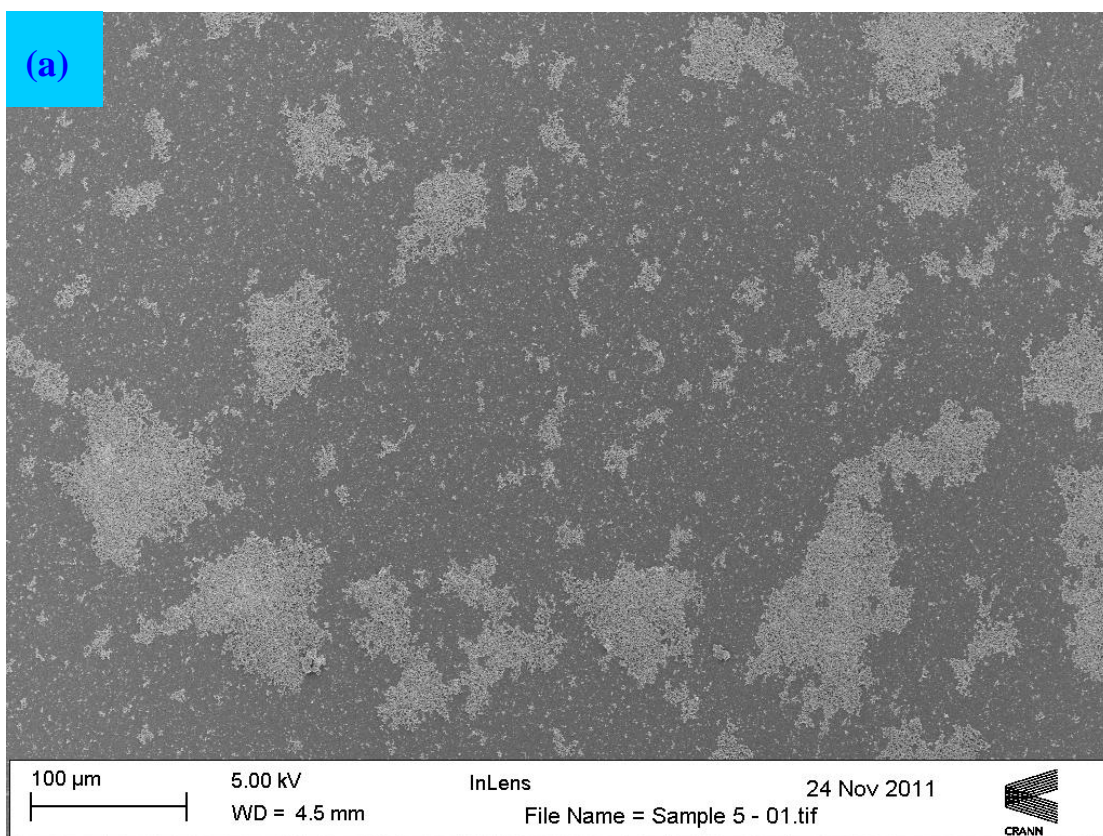


Figure S17. (a) and (b) SEM images of the dried sample obtained by liquefying the metal-organic gels **6** using methanol (SEM sample preparation C).

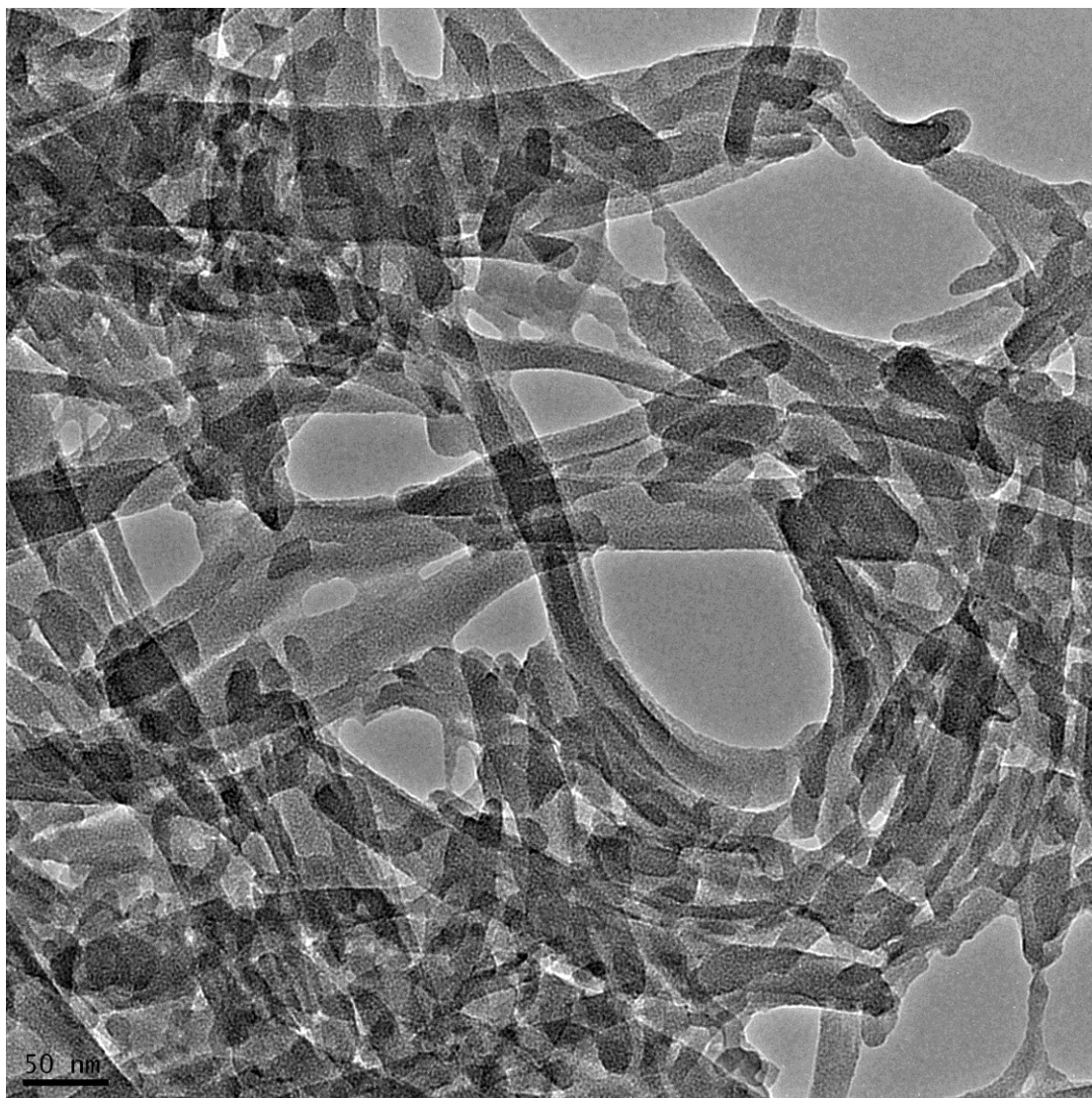


Figure S18. TEM image of dried metal-organic gel **6**.

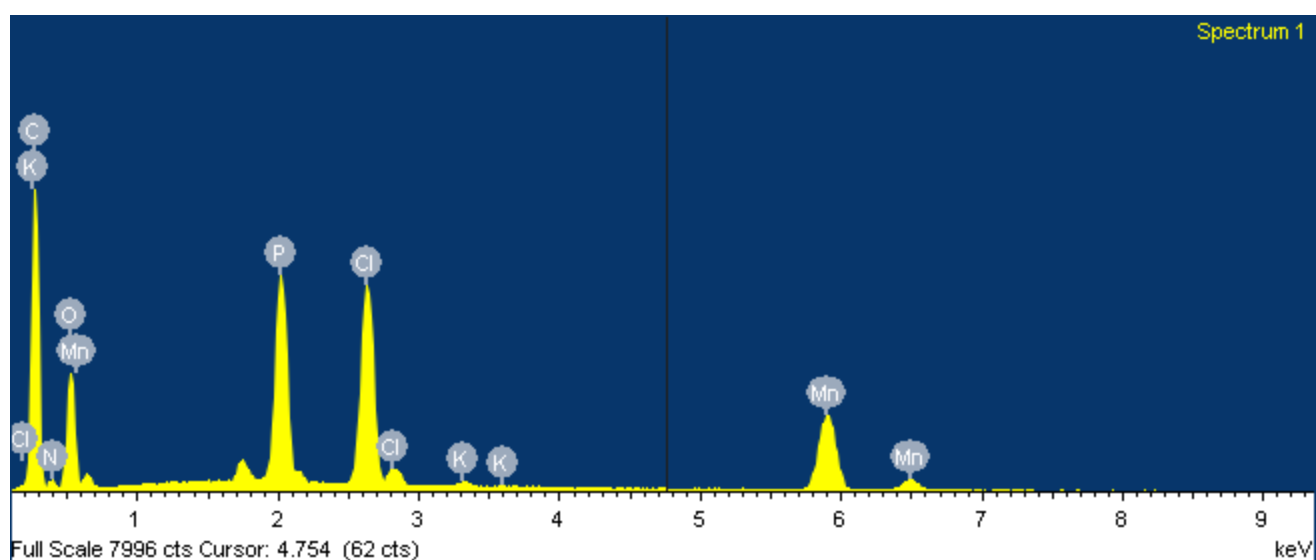
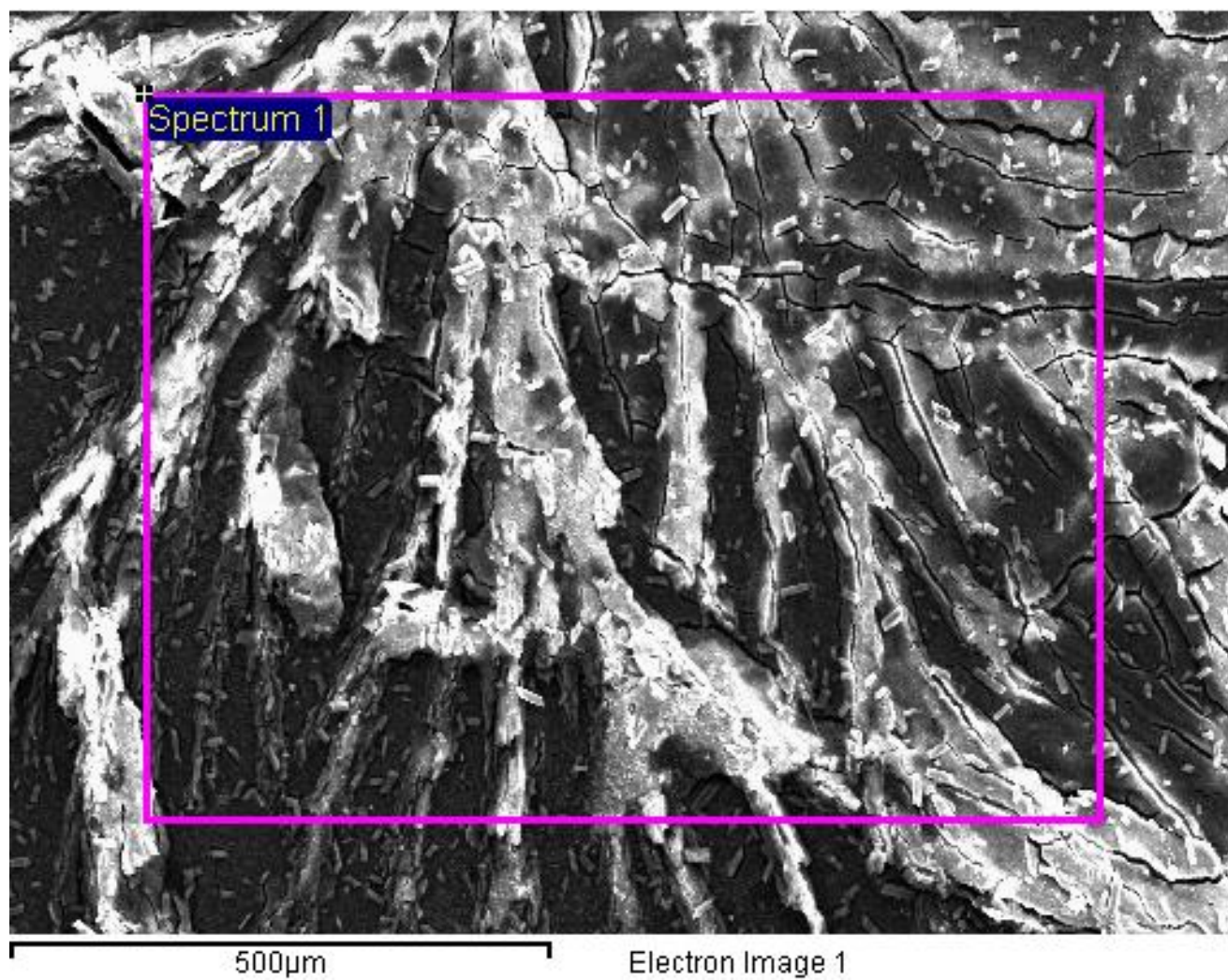


Figure S19. EDX spectra images of the dried metal-organic gel **6** (SEM sample preparation **A**).