Crystalline assembly of metal-organic polyhedra driven by ionic interactions with polyoxometalates

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Material and methods

<u>Synthesis of **SiM**₁₂; 4 TBA⁺ (M = Mo or W, TBA⁺: tetrabutylammonium)</u>

 $(TBA)_4SiMo_{12}O_{40}$ and $(TBA)_4SiW_{12}O_{40}$ were prepared according to literature,¹ by treatment of solutions of commercial silicomolybdic acid $(H_4SiW_{12}O_{40})$ or silicotungstic acid $(H_4SiW_{12}O_{40})$ with saturated aqueous solutions of tetrabutylammonium bromide. The solids formed were filtered and washed abundantly with water, then recrystallized in acetonitrile.

Synthesis of ZrBDC; 4 OTf

Formula: { $[Cp_3Zr_3(\mu_3-O)(\mu_2-OH)_3]_4(BDC)_6$ }⁴⁺; 4 OTf (Cp: = cyclopentadienyl; BDC: benzene-1,4-dicarboxylate; OTf: trifluoromethanesulfonate)

This synthesis was adapted from literature.^{2,3} Zirconocene dichloride (5.10 g, 17.5 mmol) and terephthalic acid (1.45 g, 8.7 mmol) were dissolved in 150 ml N,N-dimethylformamide and 5 ml water, and kept at 65 °C for 16 h. After reaction, the solvent was filtered out, and the white crystals (**ZrBDC**; 4 Cl⁻) where washed with DMF and diethyl ether before being introduced in a round bottom flask of known mass and degassed (0.3 kPa) for 16 h at 120 °C. After degassing, the mass of **ZrBDC**; 4 Cl⁻ was determined (ca. 3.3 g), and silver triflate (AgOTf, 4.4 equivalent per ZrBDC, 1.14 g in this case) and methanol (150 ml) were introduced in the flask, and the reaction was wrapped in aluminum foil and kept stirred at room temperature for 3 days. After reaction, the AgCl precipitate was removed by coarse filtration (pore size: 5 µm) then by centrifugation (14000 rpm) and filtration on a PTFE membrane $(0.1 \,\mu\text{m})$, until a clear solution was obtained. Toluene (about 100 ml) was then added to the solution, and methanol was removed selectively with a rotary evaporator (150 kPa, 40 °C), taking care of avoiding complete drying by adding more toluene if needed. Once most of the methanol was removed, a white precipitate appeared in the flask, then was filtered, washed abundantly with toluene then n-hexane, and degassed, yielding 3.5 g of **ZrBDC**; 4 OTf. Yield: 65%. ¹NMR (600 MHz, DMSO-d₆): 10.43 ppm (s, 12 H, μ_2 -OH); 7.93 ppm (s, 24 H, BDC); 6.59 ppm (s, 60 H, Cp).

Synthesis of ZrNDC; 4 OTF

Formula: { $[Cp_3Zr_3(\mu_3-0)(\mu_2-OH)_3]_4(NDC)_6$ }⁴⁺; 4 OTf (NDC: naphthalene-2,6-dicarboxylate)

This synthesis was adapted from literature.^{2,3} Zirconocene dichloride (2.78 g, 9.5 mmol) and 2,6-naphthalenedicarboxylic acid (1.38 g, 4.8 mmol) were dissolved in 160 ml N,N-dimethylformamide and 24 ml water, and kept at 65 °C for 16 h. After reaction, the solvent was filtered out, and the white crystals (**ZrNDC**; 4 Cl⁻) where washed with DMF and diethyl

ether before being introduced in a round bottom flask of known mass and degassed (0.3 kPa) for 16 h at 120 °C. After degassing, the mass of **ZrNDC**; 4 Cl⁻ was determined (ca. 1.5 g), and silver triflate (AgOTf, 4.4 equivalent per **ZrNDC**, 0.47 g in this case) and methanol (150 ml) were introduced in the flask, and the reaction was wrapped in aluminum foil and kept stirred at room temperature for 3 days. After reaction, the AgCl precipitate was removed by coarse filtration (pore size: 5 μ m) then by centrifugation (14000 rpm) and filtration on a PTFE membrane (0.1 μ m), until a clear solution was obtained. Toluene (about 100 ml) was then added to the solution, and methanol was removed selectively with a rotary evaporator (150 kPa, 40 °C), taking care of avoiding complete drying by adding more toluene if needed. Once most of the methanol was removed, a white precipitate appeared in the flask, then was filtered, washed abundantly with toluene then n-hexane, and degassed, yielding 1.40 g of **ZrNDC**; 4 OTf. Yield: 44%. ¹NMR (600 MHz, DMSO-d₆): 10.25 ppm (s, 12 H, μ ₂-OH); 8.53 ppm (s, 12 H, NDC); 8.02-7.96 ppm (m, 24 H, NDC); 6.70 ppm (s, 60 H, Cp).

Synthesis of ZrBDC-SiMo12

Formula: {[Cp₃Zr₃(μ_3 -0)(μ_2 -OH)₃]₄(BDC)₆}⁴⁺; SiMo₁₂O₄₀⁴⁻

300 mg **ZrBDC**; 40Tf (8.05 mmol) was introduced in a 50 ml vial, then dissolved in a mixture of methanol (5 ml) and acetonitrile (15 ml). **SiMo**₁₂; 4TBA⁺ (148 mg, 0.66 equivalent per MOP) was introduced in a 25 ml vial, then dissolved in a mixture of methanol (5 ml) and acetonitrile (15 ml), using ultrasonication. The **SiMo**₁₂ solution was then added dropwise to the **ZrBDC** solution under vigorous stirring, over the course of 15 minutes. A yellow precipitate formed instantly upon mixing. After addition, the suspension was kept 30 min under stirring, then let to rest for 24 h at room temperature. Precipitation is quantitative with regard to **SiMo**₁₂, as manifested by the absence of color in the supernatant. The solid was then filtered, washed abundantly with a methanol/acetonitrile mixture (1:3 (w/w)) then dried with a nitrogen flow to produce ca. 290 mg of a yellow solid (solvated **ZrBDC**-**SiMo**₁₂). **ZrBDC-SiMo**₁₂ was kept with residual solvent in the pores (ca. 10 w%) to prevent crystallinity loss.

Synthesis of ZrBDC-SiW₁₂

Formula: {[Cp₃Zr₃(µ₃-O)(µ₂-OH)₃]₄(BDC)₆}⁴⁺; SiW₁₂O₄₀⁴⁻

300 mg **ZrBDC**; 40Tf (8.05 mmol) was introduced in a 50 ml vial, then dissolved in a mixture of methanol (5 ml) and acetonitrile (15 ml). **SiW**₁₂; 4TBA⁺ (204 mg, 0.66 equivalent per MOP) was introduced in a 25 ml vial, then dissolved in a mixture of methanol (5 ml) and acetonitrile (15 ml), using ultrasonication. The **SiW**₁₂ solution was then added dropwise to the **ZrBDC** solution under vigorous stirring, over the course of 15 minutes. A white precipitate formed instantly upon mixing. After addition, the suspension was kept 30 min under stirring, then let to rest for 24 h at room temperature. The solid was then filtered, washed abundantly with a methanol/acetonitrile mixture (1:3 (w/w)) then dried with a nitrogen flow to produce ca. 350 mg of a white solid (solvated **ZrBDC-SiW**₁₂). **ZrBDC-SiW**₁₂ was kept with residual solvent in the pores (ca. 10 w%) to prevent crystallinity loss.

Synthesis of ZrNDC-SiMo₁₂

Formula: {[Cp₃Zr₃(µ₃-0)(µ₂-0H)₃]₄(NDC)₆}⁴⁺; SiMo₁₂O₄₀⁴⁻

300 mg **ZrNDC**; 40Tf (7.45 mmol) was introduced in a 50 ml vial, then dissolved in a mixture of methanol (5 ml) and acetonitrile (15 ml). **SiMo**₁₂; 4TBA⁺ (137 mg, 0.66 equivalent per MOP) was introduced in a 25 ml vial, then dissolved in a mixture of methanol (5 ml) and acetonitrile (15 ml), using ultrasonication. The **SiMo**₁₂ solution was then added dropwise to the **ZrNDC** solution under vigorous stirring, over the course of 15 minutes. A yellow precipitate formed instantly upon mixing. After addition, the suspension was kept 30 min under stirring, then let to rest for 24 h at room temperature. Precipitation is quantitative with regard to **SiMo**₁₂, as manifested by the absence of color in the supernatant. The solid was then filtered, washed abundantly with a methanol/acetonitrile mixture (1:3 (w/w)) then dried with a nitrogen flow to produce ca. 280 mg of a yellow solid (solvated **ZrNDC-SiMo**₁₂). **ZrNDC-SiMo**₁₂ was kept with residual solvent in the pores (ca. 10 w%) to prevent crystallinity loss.

Synthesis of ZrNDC-SiW₁₂

Formula: {[Cp₃Zr₃(µ₃-O)(µ₂-OH)₃]₄(NDC)₆}⁴⁺; SiW₁₂O₄₀⁴⁻

300 mg **ZrNDC**; 40Tf (7.45 mmol) was introduced in a 50 ml vial, then dissolved in a mixture of methanol (5 ml) and acetonitrile (15 ml). **SiW**₁₂; 4TBA⁺ (189 mg, 0.66 equivalent per MOP) was introduced in a 25 ml vial, then dissolved in a mixture of methanol (5 ml) and acetonitrile (15 ml), using ultrasonication. The **SiW**₁₂ solution was then added dropwise to the **ZrNDC** solution under vigorous stirring, over the course of 15 minutes. A yellow precipitate formed instantly upon mixing. After addition, the suspension was kept 30 min under stirring, then let to rest for 24 h at room temperature. The solid was then filtered, washed abundantly with a methanol/acetonitrile mixture (1:3 (w/w)) then dried with a nitrogen flow to produce ca. 340 mg of a yellow solid (solvated **ZrNDC-SiMo**₁₂). **ZrNDC-SiMo**₁₂ was kept with residual solvent in the pores (ca. 10 w%) to prevent crystallinity loss.

Reaction of ZrBDC-SiMo12 with hydrazine vapors

Freshly prepared **ZrBDC-SiMo**₁₂ (about 50 mg) and hydrazine monohydrate (about 1 ml) were placed in two separate vials and introduced together into a small vacuum desiccator. A third vial containing $(TBA)_4SiMo_{12}$ was also introduced in the desiccator, in order to provide a comparison sample submitted to the same hydrazine partial pressure. Pressure was then reduced slowly until boiling of the hydrazine monohydrate was observed, after which the vacuum tap was closed. A progressive color change of **ZrBDC-SiMo**₁₂ from yellow to dark blue was observed as hydrazine vapors diffused in the chamber. Samples were then maintained under hydrazine pressure for a given time (for instance 90 s), before air was reintroduced in the desiccator. The hydrazine vial was then removed, and samples were submitted to 5 min of dynamic vacuum in order to remove the hydrazine condensed on the vial walls.

Physical measurement

Powder X-ray diffraction (PXRD) was carried out on a Rigaku Ultima IV diffractometer with graphite monochromated Cu K α . Thermogravimetric analysis were performed on a Rigaku TG8120 Thermoplus Evo, using platinum pan and a N₂ flow of 100 ml/min. N₂ adsorption isotherms were measured on a BELSORP-max, using a Dewar bottle filled with

liquid nitrogen. CO₂ adsorption isotherms were measured on the same machine, using a water circulation bath. Heat of adsorption was determined using the Clausius-Clapeyron equation with two temperatures (283 K and 298 K). For both gases, samples were activated at 60 °C for 16 h. Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) were performed on a Hitachi SU3500. Infrared spectra were performed on a Perkin Elmer Spectrum Two FT-IR equipped with an ATR accessory, at room temperature. Solid-state UV-visible spectra were collected on a JASCO V-750, using a diffuse reflectance accessory.

Single-crystal preparation

ZrBDC-SiMo₁₂ and **ZrBDC-SiW**₁₂ were first prepared as powders as previously mentioned, then dissolved in dimethylacetamide (DMA, 10 mg/ml). The solutions were filtered to remove any solid residues. Crystals were formed by carefully layering in a narrow glass tube 0.5 ml of POM-MOP solution, then 2 ml of DMA and 2 ml of methanol and waiting for solvent diffusion. Single crystals were obtained after 3 weeks, and kept in the crystallization solvent until analysis.

Single-crystal X-ray diffraction

All single-crystal X-ray diffraction were collected on a Bruker SMART APEX II Ultra CCDdetector diffractometer, with a rotating-anode (Bruker Turbo X-ray source) with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Single-crystals were mounted on a polymer film with liquid paraffin and the temperature kept constant under flowing N2 gas. Computations were carried out on APEX2 crystallographic software package and OLEX2 software.⁴ All of the structures were solved by a standard direct method and expanded Fourier techniques (SHELXT and SHELXL). Disordered solvent in the pores were occluded using OLEX2 solvent mask procedure. Full-matrix least-squares refinements were carried out with isotropic thermal parameters for all non-disordered atoms. Relevant crystal data collection and refinement data for the crystal structures of **ZrBDC-SiMo**₁₂ and **ZrBDC-SiW**₁₂ are summarized in Table S2.



Figure S1. Thermogravimetric analysis profiles of the POM-MOP materials. Heating rate: 10 °C/min. The origin of each mass loss steps is indicated. Note that all samples had a strong tendency to graphitization and carbidization, so that mass loss are unreliable to determine composition.

Table S1. Elemental analysis data for the different POM-MOPs. The low nitrogen content confirms the replacement of TBA⁺ by MOPs as counter-cations of the POMs. Note also that Mo, W (and to a lesser extent, Zr and Si) are known to form carbides when their oxides are heated in presence graphitic carbon.⁵ The corrected expected values for C were calculated assuming WC and MoC were fully formed. The carbon depletion in the samples might thus be explained by a partial carbide formation during the analysis.

	ZrBDC-SiMo ₁₂	ZrBDC-SiW ₁₂	ZrNDC-SiMo ₁₂	ZrNDC-SiW ₁₂
C (%; Measured)	23.62	19.55	27.26	23.46
C (%; Calculated)	26.22	21.61	30.21	25.15
C (%; Corrected)	23.30	19.21	27.46	22.86
H (%; Measured)	1.76	1.36	1.88	1.51
H (%; Calculated)	1.96	1.61	2.07	1.73
N (%; Measured)	0.02	0.01	0.03	0.00
N (%; Calculated)	0.00	0.00	0.00	0.00



Figure S2. Powder diffraction patterns of $ZrBDC-SiW_{12}$ POM-MOPs prepared by mixing POMs and MOPs at different ratios. POM and MOP solutions were mixed all at once for this experiment.

	ZrBDC-SiMo ₁₂	ZrBDC-SiW ₁₂
CCDC deposition number	2059549	2059557
Formula	C ₁₀₈ O ₄₀ Zr ₁₂ ;SiMo ₁₂ O ₄₀	C ₁₀₈ O ₄₀ Zr ₁₂ ;SiW ₁₂ O ₄₀
Temperature (K)	100	100
Crystal system	Triclinic	Triclinic
Space group	P1 (2)	P1 (2)
a (Å)	20.547(3)	23.393(6)
<i>b</i> (Å)	24.403(3)	24.882(6)
<i>c</i> (Å)	31.283(4)	29.501(7)
α (°)	99.271(2)	99.888(3)
β (°)	107.416(2)	102.172(3)
γ (°)	107.007(2)	107.063(3)
V (Å ³)	13770.3	15537.2
Z	2	2
Reflections	30281	28408
GOF	1.095	1.092
R_1	8.11 %	13.6 %
wR ₂	23.22 %	37.73 %

Table S2. Crystallographic data and refinement of $ZrBDC-SiMo_{12}$ and $ZrBDC-SiW_{12}$.



Figure S3. Detail of the environment around a **SiMo**₁₂ POM in **ZrBDC-SiMo**₁₂ crystal structure. Five MOPs (identified by letters A to E) are located in the vicinity of the POM. Table S2 summarizes the distances between the POM and each cage. Note that POMs A, B and C have a "Vertex-on" configuration, while D and E have an "Edge-on" configuration.

Table S3. List of distances between a POM and the Zr-clusters of its surrounding MOPs in **ZrBDC-SiMo**₁₂. Note that cage D and E have two Zr-clusters relatively close to the POM. Distances are considered either from center to center (*i.e.* from Si to μ_3 -O), or as the minimal distance between a Mo of the POM and a C in a cyclopentadienyl ligands. The sum of van der Waals radii for Mo and C is 3.79 Å.

ZrBDC	Distance (Si to μ_3 -O, Å)	Distance (Min(Mo-C), Å)
А	9.065	4.369
В	9.186	4.300
С	9.142	4.115
D1	12.24	6.233
D2	13.147	7.045
E1	12.613	6.349
E2	14.078	7.85



Figure S4. A: Crystal structure of **ZrBDC-SiW**₁₂. B: Detail of the coordination environment around a **SiW**₁₂ POM. The structure of **ZrBDC-SiW**₁₂ is a bit different from that of **ZrBDC-SiMO**₁₂, and six MOPs can be observed at the vicinity of the POM (identified by letter from A to F). A, B and C have a "Vertex-on" configuration with a cluster very close to the POM. D has an "Edge-on" configuration. E and F have a "Vertex-on" configuration but are at slightly higher distances.

Table S4. List of distances between a POM and the Zr-clusters of its surrounding MOPs in **ZrBDC-SiW**₁₂. Note that cage D has two Zr-clusters relatively close to the POM. Distances are considered either from center to center (*i.e.* from Si to μ_3 -O), or as the minimal distance between a W of the POM and a C in a cyclopentadienyl ligands. The sum of van der Waals radii for W and C is 3.80 Å.

ZrBDC	Distance (Si to μ_3 -0, Å)	Distance (Min(W-C), Å)
А	10.207	4.522
В	9.201	4.035
С	9.207	4.16
D1	11.758	7.179
D2	14.037	8.331
E	14.727	8.453
F	14.002	7.67



Figure S5. Comparison of crystals structures and discussion on their relationship with the experimental PXRD data. The crystal structures of **ZrBDC-SiMo**₁₂ and **ZrBDC-SiW**₁₂ (**A**) reveal overall similar assemblies of POM and MOPs. However, the third POM-MOP layers is "slided" differently in those two phases. The red dotted line is aligned with two POMs, and help visualizing the relative position of the third one. **B** shows experimental patterns for bulk-prepared samples, and patterns simulated from the cif-files of crystal structures. One consequence of the different packing in the crystal structures is that the simulated PXRD patterns of these phases (crystallized in DMA/MeOH) are not identical. There is a clear peak-to-peak correspondence between the simulated **ZrBDC-SiMo**₁₂ and the experimental patterns of both **ZrBDC-SiMo**₁₂ and **ZrBDC-SiW**₁₂ bulk samples (obtained in MeCN/MeOH), revealing that the configurations are most likely very close.

The key message here is that all these POM-MOP phases are structurally close, but their exact configuration depends on the precise solvation state and set of interactions.



Figure S6. SEM-EDX element maps of **ZrBDC-SiMo**₁₂.



W M ⊣50um 200x kV:15.0 Tilt:0

ZrL ⊢--50um 200x kV:15.0 Tilt:0

Figure S7. SEM-EDX element maps of **ZrBDC-SiW**₁₂.



Figure S8. SEM-EDX element maps of ZrNDC-SiMo₁₂.



Figure S9. SEM-EDX element maps of ZrNDC-SiW₁₂.



Figure S10. Typical EDX spectrum and composition analysis of ZrBDC-SiMo₁₂.



Figure S11. Typical EDX spectrum and composition analysis of ZrBDC-SiW₁₂.

Figure S12. Typical EDX spectrum and composition analysis of ZrNDC-SiMo₁₂.

Figure S13. Typical EDX spectrum and composition analysis of ZrNDC-SiW₁₂.

Table S5. Heavy element ratios in POM-MOPs, determined by SEM-EDX. The ratios involve either Mo or W, depending on the constitutive POM. While quantitativity can reasonably be trusted for **SiMo**₁₂-based POM-MOPs, note however that some deviation might occur for **SiW**₁₂-based ones, due to the proximity of Si K α (1.740 keV) and W M (1.774 keV).

POM-MOP	EDX atomic ratio Mo/Si or W/Si	EDX atomic ratio Mo/Zr or W/Zr
ZrBDC-SiMo ₁₂	11.5 (1.3)	0.95 (0.01)
ZrBDC-SiW ₁₂	5.5 (0.6)	1.33 (0.03)
ZrNDC-SiMo ₁₂	10.4 (0.6)	1.00 (0.01)
ZrNDC-SiW ₁₂	4.8 (0.6)	1.32 (0.04)

Figure S14. FTIR spectra of **ZrBDC**-based POM-MOPs and selected compounds. By comparison, characteristic peaks of OTf⁻ and TBA⁺ can be identified. Notably: OTf⁻: 1315 to 1130 cm⁻¹ (multiple peaks); 1025 cm⁻ (doublet). TBA⁺: 3000 to 2890 cm⁻¹ (multiple peaks); 2871 cm⁻¹ (sharp); 1500 to 1430 cm⁻¹ (multiple peaks).

Characteristic peaks of **ZrBDC** and the POM can then be identified and attributed to either of the components. For instance, **ZrBDC-SiMo**₁₂ exhibited characteristic peaks of **ZrBDC** at 1549 cm⁻¹, 1392 cm⁻¹, 744 cm⁻¹ and 550 cm⁻¹, and also characteristic peaks of **SiMo**₁₂ at 952 cm⁻¹, 898 cm⁻¹ and 787 cm⁻¹. By comparison, **ZrBDC-SiW**₁₂ presented the same group of **ZrBDC**-related peaks, at the same positions, and also POM-peaks at 968 cm⁻¹, 916 cm⁻¹ and 790 cm⁻¹, slightly shifted due to the different metal in **SiW**₁₂.

Figure S15. FTIR spectra of **ZrNDC**-based POM-MOPs and selected compounds. Following the discussion of Figure S14, the characteristic peaks of **ZrNDC** can be identified at 1602 cm⁻¹, 1544 cm⁻¹, 1414 cm⁻¹, 1359 cm⁻¹, 614 cm⁻¹. POM-related peaks can also be observed at their expected positions.

Figure S16. N₂ adsorption isotherms (77 K) of POM-MOP materials (gravimetric scale). Closed symbols indicate adsorption, and open symbols, desorption.

Figure S17. N_2 adsorption isotherms (77 K) of POM-MOP materials (normalized in N_2 per cage). Closed symbols indicate adsorption, and open symbols, desorption. The dashed line corresponds to the maximum capacity of **ZrBDC**; 4Cl⁻, as reported in the literature.⁶

Figure S18. PXRD patterns of POM-MOPs materials measured after activation and $N_{\rm 2}$ adsorption experiments.

Figure S19. CO₂ adsorption isotherms of **ZrBDC**-based POM-MOP materials. Closed symbols indicate adsorption, and open symbols, desorption.

Figure S20. CO₂ adsorption isotherms of **ZrNDC**-based POM-MOP materials. Closed symbols indicate adsorption, and open symbols, desorption.

Figure S21. Heat of adsorption of CO₂ in POM-MOP materials.

Figure S22. UV-Vis spectra of $(TBA^+)_4$ SiMo₁₂ before and after 90 s exposure to hydrazine vapors. Photographs of the samples are shown in inset. Note that the absorbance band of the reduced specie at 700 nm is significantly lower than for **ZrBDC-SiMo**₁₂. In consequence, the sample appeared green, instead of dark blue.

Figure S23. (**A**, **B**) Infrared spectra of **ZrBDC-SiMo**₁₂ before and after 90 s exposure to hydrazine vapors. **A** presents the complete spectra, and **B** is a zoom in without offset, to better show peaks shifts. We refer to Figure S14 for the peak attribution. Characteristic peaks of **ZrBDC** (at 1549 cm⁻¹, 1392 cm⁻¹, 744 cm⁻¹ and 550 cm⁻¹ notably) did not change, while peaks originating from **SiMo**₁₂ shifted from 952 cm⁻¹, 898 cm⁻¹ and 787 cm⁻¹ to 933 cm⁻¹, 882 cm⁻¹ and 770 cm⁻¹ respectively. Peaks of guest solvents are also indicated. Protonated hydrazine (downshifted compared to hydrazine hydrate)⁷ can be detected. The protons originate from the oxidation of hydrazine (formally, N₂H₄ \rightarrow N₂ + 4 H⁺ + 4 e⁻), and compensate the charge of the reduced POMs (SiMo₁₂O₄₀⁵⁻).

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