ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)
FOR

Intrinsically Porous Molecular Building Blocks for Metal Organic Frameworks
Tailored by the Bridging Effect of Counter Cations

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Materials and Physical Measurements

All reagents were purchased from commercial sources and used without further purification. The FT-IR spectra were recorded on KBr disk using a Nicolet-Avatar 370 spectrometer between 400 and 4000 cm\textsuperscript{-1}. Elemental analyses: CHN microanalyses were performed on a Perkin-Elmer 240C elemental analyser, and ICP-OES analyses were carried out on a PerkinElmer Optima 8300 optical emission spectrometer. Thermogravimetric analyses were carried out on a TA Instruments SDT Q600 thermobalance with a 100 mL min\textsuperscript{-1} flow of nitrogen; the temperature was ramped from 20 °C to 800 °C at a rate of 5 °C min\textsuperscript{-1}. Powder X-ray diffraction (PXRD) patterns were obtained using a Bruker D8 ADVANCE diffractometer with Cu K\textalpha radiation (\lambda = 1.54056 Å). The NMR spectra were recorded on a Bruker Avance III 400 MHz instrument at room temperature, using 5 mm tubes for $^1$H, $^{13}$C, and $^{31}$P with respective resonance frequencies of 399.78 MHz ($^1$H), 100.71 MHz ($^{13}$C), and 162.14 MHz ($^{31}$P). The chemical shifts are reported with respect to the references Si(CH$_3$)$_4$ ($^1$H and $^{13}$C) and 85% H$_3$PO$_4$ ($^{31}$P).

X-ray Crystallography

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Crystal data for the seven compounds were collected at 150 K on a Bruker D8 Venture APEX CCD single-crystal diffractometer equipped with a sealed Mo tube and a graphite monochromator ($\lambda = 0.71073$ Å). The crystals were mounted in a Hampton cryoloop with light oil to prevent loss of crystal waters. The SHELX software package (Bruker)[1] was used to solve and refine the structures. An empirical absorption correction was applied using the SADABS program.[2] The structures were solved by direct methods and refined by the full-matrix least-squares method ($\sum w(|F_o|^2 - |F_c|^2)^2$) with anisotropic thermal parameters for all heavy atoms included in the model. It was impossible to locate all counter cations by XRD, due to crystallographic disorder, and it was also impossible to locate hydrogens of crystal waters, which are common issues in polyoxometalate crystallography. The hydrogen atoms of cyclodextrins and acetates were introduced in geometrically calculated positions. Finally, the exact number of counter cations and crystal waters in the formulas were based on elemental analysis, and used throughout the manuscript for consistency.

The crystal data and structure refinement for the seven compounds are summarized in Table S1. Further details on the crystal structure investigation may be obtained from the CCDC-1963904 (Na-PMo-α-CD), CCDC-1963902 (K-PMo-α-CD), CCDC-1963899 (Cs-PMo-α-CD), CCDC-1963905 (Na-PMo-β-CD), CCDC-1963906 (Na-PMo-γ-CD), CCDC-1963903 (K-PMo-γ-CD), CCDC-1963900 (Cs-PMo-γ-CD), which contain the supplementary crystallographic data for this paper.

**Elemental Analysis**

**Na-PMo-α-CD (%)**: Calcd: Na 5.42, P 2.65, Mo 20.58, C 20.36; Found: Na 5.33, P 2.56, Mo 20.25, C 20.66.

**K-PMo-α-CD (%)**: Calcd: K 5.05, Na 2.58, P 2.78, Mo 21.55, C 19.70; Found: K 4.99, Na 2.56, P 2.81, Mo 21.49, C 19.52.

**Cs-PMo-α-CD (%)**: Calcd: Cs 11.45, Na 2.64, P 2.37, Mo 18.37, C 17.94; Found: Cs 11.38, Na 2.60, P 2.37, Mo 18.21, C 18.08.

**Na-PMo-β-CD (%)**: Calcd: Na 5.06, P 2.60, Mo 20.11, C 21.65; Found: Na 5.12, P 2.54, Mo 20.04, C 21.53.

**Na-PMo-γ-CD (%)**: Calcd: Na 7.75, P 2.98, Mo 23.11, C 15.91; Found: Na 7.75, P 3.03, Mo 23.10, C 16.03.

**K-PMo-γ-CD (%)**: Calcd: K 9.71, Na 0.57, P 3.07, Mo 23.84, C 14.92; Found: K 9.41, Na 0.51, P 2.97, Mo 23.14, C 15.03.

**Cs-PMo-γ-CD (%)**: Calcd: Cs 15.12, Na 2.85, P 2.56, Mo 19.85, C 13.42; Found: Cs 15.19, Na 2.76, P 2.57, Mo 19.88, C 13.28.

**FT-IR Spectroscopy**
FT-IR spectra recorded for the seven compounds are presented in Figure S3-S5, S13-S16. For all spectra, the strong absorption band of O–H bonds of cyclodextrins appears at ~3400 cm\(^{-1}\). The peak centered at ~2930 cm\(^{-1}\) corresponds to the asymmetrical stretching vibration of C–H bonds while the band at ~1640 cm\(^{-1}\) comes from the C–C stretching of polysaccharides. The peaks present in the region from 1480 to 1180 cm\(^{-1}\) are related to the C–H bending vibrations while the band located between 1160 – 1040 cm\(^{-1}\) is characteristic of the symmetrical stretching of glycosidic C–O–C and C–O bonds in polysaccharides.\(^3\) Besides, a characteristic absorption band centered at 1032 cm\(^{-1}\) is typical for P–O bonds. The peaks that are below 1000 cm\(^{-1}\) can be assigned to the terminal Mo=O bonds as well as the bridging Mo–O–Mo bond stretching modes.

**Thermogravimetric Analysis**

Thermogravimetric analyses (TGA) were performed on crystalline samples under nitrogen flow, and three weight-loss steps were observed for all seven samples (Figures S17-S23). Taking Na-PMo-γ-CD as an example, the first weight loss step of 12.2% represents a dehydration process up to around 160 °C, resulting in loss of 56 crystal water molecules (calc. 12.1%). Further weight loss covering the temperature range from 220 to 800 °C is largely due to the loss of organic moieties and structural reorganization of the polyanion.

**Powder XRD**

Powder X-ray diffraction patterns measured for the seven compounds are in agreement with the simulated results from the respective single crystal XRD data (Figures S24-S29).

**References**

1. Sheldrick, G. M. A short history of SHELX. *Acta Crystallogr., Sect. A: Found. Crystallogr.* A64, 112–122 (2008).
2. Sheldrick, G. M. SADABS, Program for empirical X-ray absorption correction (Bruker-Nonius: Madison, WI, 1990).
3. Socrates, G. Infrared and Raman Characteristic Group Frequencies (John Wiley & Sons Ltd, United Kingdom, 3rd edn, 2001).

**Table S1.** Crystal data and structure refinement for the seven as-made PMo-CD MOFs.
|                        | Na-PMo-α-CD                                      | K-PMo-α-CD                                      |
|------------------------|-------------------------------------------------|------------------------------------------------|
| Empirical formula      | $Na_{21}C_{152}H_{183}O_{266}P_8Mo_{20}$        | $K_{11.5}Na_{3}C_{144}H_{156}O_{239}P_8Mo_{20}$ |
| Formula weight (g/mol) | 8915.32                                         | 8395.86                                         |
| Crystal system, space group | Triclinic, $P\overline{1}$                  | Monoclinic, $P\overline{2}_1$                |
|                        | $a = 16.4104(10)$ Å, $a = 82.942(2)^\circ$     | $a = 16.3345(7)$ Å,                           |
|                        | $b = 22.5164(13)$ Å, $\beta = 70.254(2)^\circ$ | $b = 43.3770(19)$ Å, $\beta = 93.656 (18)^\circ$ |
|                        | $c = 24.1911(16)$ Å, $\gamma = 82.498(2)^\circ$ | $c = 22.8979$ Å,                              |
| Volume (Å$^3$)         | 8311.3(9)                                       | 16191.1(13)                                    |
| Z, calculated density (g/cm$^3$) | 1, 1.781                                        | 2, 1.722                                        |
| $F(000)$               | 4414                                            | 8287                                           |
| Absorption coefficient (mm$^{-1}$) | 0.917                                      | 1.053                                           |
| Absorption correction  | Multi-scan                                      | Multi-scan                                      |
| $\theta$ range for data collection | 3.89–49.998°                                   | 3.676–50°                                      |
| Limiting indices       | -19 ≤ h ≤ 19, -26 ≤ k ≤ 26,                    | -19 ≤ h ≤ 19, -51 ≤ k ≤ 51,                   |
|                        | -28 ≤ l ≤ 28                                    | -27 ≤ l ≤ 27                                   |
| Reflection collected / unique / $R_{int}$ | 508794 / 58431 / 0.0336 | 398850 / 56977 / 0.0413                        |
| Completeness to $\theta_{max}$ | 99.8 %                                          | 99.9 %                                         |
| Data / restraints / parameters | 58431 / 17178 / 4305                              | 56977 / 13591 / 3989                           |
| Final $R$ indices $[I > 2\sigma(I)]$ | $R_1[^a] = 0.0420$, $wR_2[^b] = 0.1085$              | $R_1[^a] = 0.0531$, $wR_2 = 0.1458$             |
| Final $R$ indices (all data) | $R_1[^a] = 0.0427$, $wR_2[^b] = 0.1090$              | $R_1[^a] = 0.0551$, $wR_2[^b] = 0.1478$         |
| Goodness-of-fit        | 1.033                                           | 1.028                                          |
| Largest diff. peak and hole (e/Å$^3$) | 3.34 and -1.86                               | 3.32 and -1.53                                 |

[^a] $R_1 = \Sigma||F_o|| - |F_c||/\Sigma|F_o||$.  
[^b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_c^2)^2]^{1/2}$.
| Property                                      | Value                          | Value                          |
|-----------------------------------------------|-------------------------------|-------------------------------|
| **Empirical formula**                         | Cs<sub>4.5</sub>Na<sub>2.5</sub>C<sub>72</sub>H<sub>72</sub>O<sub>110.5</sub>P<sub>4</sub>Mo<sub>10</sub> | Na<sub>17</sub>C<sub>168</sub>H<sub>192</sub>O<sub>265</sub>P<sub>8</sub>Mo<sub>20</sub> |
| **Formula weight (g/mol)**                    | 4444.14                       | 9008.59                       |
| **Crystal system, space group**               | Orthorhombic, P<sub>2</sub>₁<sub>1</sub>₂<sub>1</sub>₂<sub>1</sub> | Triclinic, P1                 |
| **Unit cell dimensions**                      |                               |                               |
| a = 16.4079(8) Å, α = 100.808(3)°             | b = 23.885(2) Å, β = 95.617(3)° | c = 23.974(2) Å, γ = 91.227(3)° |
| **Volume (Å³)**                               | 15855.1(13)                   | 9102.2(14)                    |
| **Z, calculated density (g/cm³)**             | 4, 1.862                      | 1, 1.643                      |
| **F(000)**                                    | 8572                          | 4467                          |
| **Absorption coefficient (mm⁻¹)**             | 1.938                         | 0.834                         |
| **Absorption correction**                     | Multi-scan                    | Multi-scan                    |
| **θ range for data collection**               | 4.412–50°                     | 4.076–50°                     |
| **Limiting indices**                          | -19 ≤ h ≤ 19, -26 ≤ k ≤ 26,   | -19 ≤ h ≤ 19, -28 ≤ k ≤ 28,  |
| **Reflection collected / unique / R<sub>int</sub>** | 400360 / 27824 / 0.0317       | 452139 / 63722 / 0.0369       |
| **Completeness to θ<sub>max</sub>**           | 99.5 %                        | 99.8 %                        |
| **Data / restraints / parameters**            | 27824 / 5397 / 1919           | 63722 / 15525 / 4334          |
| **Final R indices [I > 2σ(I)]**               | R<sub>i</sub>[a] = 0.0465, wR<sub>2</sub>[b] = 0.1306 | R<sub>i</sub>[a] = 0.0671, wR<sub>2</sub> = 0.1833 |
| **Final R indices (all data)**                | R<sub>i</sub>[a] = 0.0469, wR<sub>2</sub>[b] = 0.1310 | R<sub>i</sub>[a] = 0.0680, wR<sub>2</sub> = 0.1842 |
| **Goodness-of-fit**                           | 1.044                         | 1.037                         |
| **Largest diff. peak and hole (e/Å³)**        | 2.52 and -1.64               | 2.52 and -1.05                |

[a] R<sub>i</sub> = Σ||F<sub>o</sub>|| - |F<sub>c</sub>||/Σ||F<sub>o</sub||. [b] wR<sub>2</sub> = [Σw(F<sub>o</sub>² - F<sub>c</sub>²)²/Σw(F<sub>o</sub>²)]<sup>1/2</sup>. 
|                      | Na-PMo-γ-CD                      | K-PMo-γ-CD                      |
|----------------------|----------------------------------|----------------------------------|
| Empirical formula    | Na$_{23}$C$_{96}$H$_{114}$O$_{210.5}$P$_8$Mo$_{20}$ | K$_{20}$Na$_{1.5}$C$_{96}$H$_{110}$O$_{193}$P$_8$Mo$_{20}$ |
| Formula weight (g/mol) | 7331.19                         | 7334.88                         |
| Crystal system, space group | Monoclinic, C2                   | Monoclinic, I2                  |
|                      | $a = 44.727(3)$ Å               | $a = 36.048(2)$ Å              |
|                      | $b = 17.6015(10)$ Å, $\beta = 92.424(2)^\circ$ | $b = 16.1202(9)$ Å, $\beta = 111.956(4)^\circ$ |
|                      | $c = 32.7474(18)$ Å             | $c = 47.517(3)$ Å              |
|                      | Volume (Å$^3$)                   | 25758(3)                        | 25609(3)                        |
|                      | Z, calculated density (g/cm$^3$) | 4, 1.890                        | 4, 1.902                        |
|                      | $F(000)$                         | 14348                           | 14346                           |
|                      | Absorption coefficient (mm$^{-1}$) | 1.149                           | 1.435                           |
|                      | Absorption correction           | Multi-scan                      | Multi-scan                      |
|                      | $\theta$ range for data collection | 3.734–50$^\circ$               | 3.752–50$^\circ$               |
|                      | Limiting indices                | -53 $\leq h \leq$ 52, -20 $\leq k \leq$ 20, | -42 $\leq h \leq$ 42, -19 $\leq k \leq$ 19, |
|                      |                                  | -38 $\leq l \leq$ 38           | -56 $\leq l \leq$ 56          |
|                      | Reflection collected / unique / $R_{\text{int}}$ | 423375 / 45126 / 0.0588         | 396465 / 45079 / 0.0357        |
|                      | Completeness to $\theta_{\text{max}}$ | 99.5 %                          | 99.9 %                          |
|                      | Data / restraints / parameters   | 45126 / 16927 / 3236            | 45079 / 14615 / 3091           |
|                      | Final $R$ indices [$I > 2\sigma(I)$] | $R_1^{[a]} = 0.0524, wR_2^{[b]} = 0.1406$ | $R_1^{[a]} = 0.0449, wR_2 = 0.1223$ |
|                      | Final $R$ indices (all data)     | $R_1^{[a]} = 0.0530, wR_2^{[b]} = 0.1412$ | $R_1^{[a]} = 0.0454, wR_2^{[b]} = 0.1226$ |
|                      | Goodness-of-fit                  | 1.032                           | 1.067                           |
|                      | Largest diff. peak and hole (e/Å$^3$) | 2.27 and -1.48                 | 3.24 and -2.06                 |

$^{[a]} R_1 = \Sigma||F_o|| - |F_c||/\Sigma|F_o|$. $^{[b]} wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. 
| **Cs-PMo-γ-CD** |
|------------------|
| **Empirical formula** | Cs$_{5.5}$Na$_6$C$_{48}$H$_{60}$O$_{102}$P$_4$Mo$_{10}$ |
| **Formula weight (g/mol)** | 4221.18 |
| **Crystal system, space group** | Monoclinic, $I2$ |
| | $a = 19.0337(7)$ Å, |
| **Unit cell dimensions** | $b = 16.6107(5)$ Å, $\beta = 93.491(2)^\circ$ |
| | $c = 43.9445(16)$ Å, |
| **Volume ($\text{Å}^3$)** | 13867.8(8) |
| **Z, calculated density (g/cm$^3$)** | 4, 2.022 |
| **F(000)** | 8050 |
| **Absorption coefficient (mm$^{-1}$)** | 2.470 |
| **Absorption correction** | Multi-scan |
| **$\theta$ range for data collection** | 4.568–50$^\circ$ |
| **Limiting indices** | $-22 \leq h \leq 22$, $-19 \leq k \leq 19$, |
| | $-52 \leq l \leq 52$ |
| **Reflection collected / unique / $R_{int}$** | 160607 / 24356 / 0.0260 |
| **Completeness to $\theta_{\text{max}}$** | 99.8 % |
| **Data / restraints / parameters** | 24356 / 2797 / 1626 |
| **Final $R$ indices [$I > 2\sigma(I)$]** | $R_1[\text{a}] = 0.0320$, $wR_2[\text{b}] = 0.0904$ |
| **Final $R$ indices (all data)** | $R_1[\text{a}] = 0.0325$, $wR_2[\text{b}] = 0.0907$ |
| **Goodness-of-fit** | 1.034 |
| **Largest diff. peak and hole (e/Å$^3$)** | 2.35 and -1.66 |
**Figure S1.** a) Chains composed of P$_2$Mo$_5$ and α-CDs stabilized by hydrogen bonds (yellow dotted lines); b) space-filling representation of Na-PMo-α-CD. Color code is the same as in Figure 1.

**Figure S2.** Guest molecules of HOAc accommodated inside the CD chain.
Figure S3. FT-IR spectrum of Na-PMo-α-CD (2% KBr pellet, v/cm⁻¹): 3417 (s), 2929 (w), 1710 (w), 1643 (m), 1564 (w), 1411 (m), 1332 (w), 1298 (w), 1244 (w), 1153 (s), 1078 (m), 1032 (s), 918 (s), 704 (s), 575 (w), 528 (w).

Figure S4. FT-IR spectrum of K-PMo-α-CD (2% KBr pellet, v/cm⁻¹): 3402 (s), 2929 (w), 1710 (w), 1641 (m), 1411 (m), 1332 (w), 1298 (w), 1244 (w), 1155 (s), 1078 (w), 1032 (s), 920 (s), 704 (s), 575 (w), 530 (w).
Figure S5. FT-IR spectrum of Cs-PMo-α-CD (2% KBr pellet, v/cm⁻¹): 3390 (s), 2929 (w), 1710 (w), 1641 (m), 1410 (m), 1329 (w), 1298 (w), 1246 (w), 1153 (s), 1030 (s), 920 (s), 702 (s), 575 (w), 528 (w).
Figure S6. $^1$H NMR spectra of Na/K-PMo-$\alpha$-CD, Na-PMo-$\beta$-CD, and Na/K-PMo-$\gamma$-CD recorded in D$_2$O at room temperature.

Figure S7. $^{13}$C NMR spectrum of Na-PMo-$\alpha$-CD recorded in D$_2$O at room temperature.
Figure S8. $^{13}$C NMR spectrum of K-PMo-α-CD recorded in D$_2$O at room temperature.

Figure S9. $^{13}$C NMR spectrum of Na-PMo-β-CD recorded in D$_2$O at room temperature.
Figure S10. $^{13}$C NMR spectrum of Na-PMo-γ-CD recorded in D$_2$O at room temperature.

Figure S11. $^{13}$C NMR spectrum of K-PMo-γ-CD recorded in D$_2$O at room temperature.
**Figure S12.** PXRD patterns of Cs-PMo-γ-CD.

**Figure S13.** FT-IR spectrum of Na-PMo-β-CD (2% KBr pellet, ν/cm⁻¹): 3427 (s), 2929 (w), 1641 (m), 1415 (m), 1369 (w), 1334 (w), 1157 (s), 1028 (s), 920 (s), 702 (s), 579 (w), 532 (w).
Figure S14. FT-IR spectrum of Na-PMo-γ-CD (2% KBr pellet, v/cm⁻¹): 3423 (s), 2931 (w), 1641 (m), 1564 (w), 1413 (m), 1371 (w), 1338 (w), 1305 (w), 1157 (s), 1026 (s), 920 (s), 702 (s), 584 (w), 526 (w).

Figure S15. FT-IR spectrum of K-PMo-γ-CD (2% KBr pellet, v/cm⁻¹): 3407 (s), 2927 (w), 1637 (m), 1417 (m), 1373 (w), 1340 (m), 1160 (s), 1078 (m), 1026 (s), 918 (s), 704 (s), 582 (w), 526 (w).
Figure S16. FT-IR spectrum of Cs-PMo-γ-CD (2% KBr pellet, v/cm⁻¹): 3415 (s), 2931 (w), 1639 (m), 1417 (m), 1338 (w), 1303 (w), 1160 (s), 1108 (w), 1026 (s), 920 (s), 704 (s), 584 (w), 530 (w).

Figure S17. Thermogram of Na-PMo-α-CD from 20 to 800 °C under N₂ atmosphere.
Figure S18. Thermogram of K-PMo-α-CD from 20 to 800 °C under N₂ atmosphere.

Figure S19. Thermogram of Cs-PMo-α-CD from 20 to 800 °C under N₂ atmosphere.
Figure S20. Thermogram of Na-PMo-β-CD from 20 to 800 °C under N₂ atmosphere.

Figure S21. Thermogram of Na-PMo-γ-CD from 20 to 800 °C under N₂ atmosphere.
Figure S22. Thermogram of K-PMo-γ-CD from 20 to 800 °C under N₂ atmosphere.

Figure S23. Thermogram of Cs-PMo-γ-CD from 20 to 800 °C under N₂ atmosphere.
Figure S24. PXRD patterns of Na-PMo-α-CD.

Figure S25. PXRD patterns of K-PMo-α-CD.
Figure S26. PXRD patterns of Cs-PMo-α-CD.

Figure S27. PXRD patterns of Na-PMo-β-CD.
Figure S28. PXRD patterns of Na-PMo-γ-CD.

Figure S29. PXRD patterns of K-PMo-γ-CD.
Figure S30. $^{31}$P NMR spectra of Na/K-PMo-α-CD, Na-PMo-β-CD, and Na/K-PMo-γ-CD recorded in D$_2$O at room temperature.