Supplementary Information

\[\text{[Ni(C}_{17}\text{H}_{20}\text{N}_{4})_4]\text{[H}_5\text{PMo}_{8}\text{V}_{18}\text{O}_{40}(\text{V}_{\text{IV}}\text{O})_2]\cdot 8\text{H}_2\text{O}:\] confinement of heteropoly anions in Ni-containing rigid concave surfaces with high catalytic activity in the oxidation of styrene

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Details for catalytic activity experiments:

The oxidation of styrene was performed in a 50 ml double necked round bottom flask fitted in a water cooled condenser and a magnetic stirrer. 13 mmol styrene, 15 ml solvent (CH$_3$CN) and 100 mg title compound were mixed in the flask and kept the temperature at 333 K, then 36 mmol dilute hydrogen peroxide (30%) was added to the flask. The mixture was analyzed by a gas chromatograph (GC-6890, FID; 30 m × 0.32 mm capillary column) after 3h reaction. The major products obtained were benzaldehyde and small amount of epoxide and benzoic acid with the conversion of styrene was 90% and the selectivity of benzaldehyde, epoxide and benzoic acid in the oxidation of styrene were 69.7%, 3.9% and 26.4%, respectively.

![Diagram](image)

**Fig. S1** A view of the discrete acyclic water pentamer in 1.
**Fig. S2** The TG curve of compound 1.

IR spectrum: 3414 cm\(^{-1}\), \(\nu\)(O-H); 1619 cm\(^{-1}\), 1383 cm\(^{-1}\), \(\nu\)(C-C), \(\nu\)(C-N); 1081 cm\(^{-1}\), \(\nu\)(P-O); 940 cm\(^{-1}\), \(\nu\)(Mo=O); 781 cm\(^{-1}\), \(\nu\)(Mo-O-Mo); 620 cm\(^{-1}\), \(\nu\)(Mo-O)

**Fig. S3** IR spectra of compound 1.

**Table S1** The O···O distances and O···O···O angles in water pentamer of 1.

<table>
<thead>
<tr>
<th>Distance</th>
<th>O···O distance (Å)</th>
</tr>
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<tbody>
<tr>
<td>O1W···O3W</td>
<td>2.740(14)Å</td>
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<tr>
<td>O3W···O4W</td>
<td>2.693(78)Å</td>
</tr>
<tr>
<td>O1W···O3W···O4W</td>
<td>101.136(376)°</td>
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<tr>
<td>O3W···O4W···O2W</td>
<td>101.608(308)°</td>
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<table>
<thead>
<tr>
<th>Distance</th>
<th>O···O···O angle (°)</th>
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<tbody>
<tr>
<td>O4W···O2W···O5W</td>
<td>86.623(337)°</td>
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**Table S2** Selected bond lengths (Å) for 1

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<th>Atom</th>
<th>Bond Length (Å)</th>
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<td>Mo(1)-O(15)</td>
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<td>Bond</td>
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Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z-1/2    #2 x,y-1,z    #3 x,y+1,z