Supporting Information for

One novel 3-D vanadoborate with unusual 3-D Na-O-Na network

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Table S1 Ranges of some important bond lengths (Å) and angles (°) for 1.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Range (Å/°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V-O</td>
<td>1.6201(10)-2.0184(8)</td>
</tr>
<tr>
<td>Na-O</td>
<td>2.265(3)-2.8427(13)</td>
</tr>
<tr>
<td>O-V-O</td>
<td>77.65(4)-147.00(3)</td>
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<tr>
<td>O-B-O</td>
<td>106.17(8)-123.39(11)</td>
</tr>
<tr>
<td>O-Na-O</td>
<td>54.21(3)-172.55(3)</td>
</tr>
</tbody>
</table>

Fig. S1. Simulated and experimental powder XRD patterns of 1.

Fig. S2. The coordination environment of Na1, Na2, Na3, and Na4 ions.
Fig. S3. The aperture of 14-ring.

Fig. S4 UV-vis absorption spectrum of 1.
Fig. S5 IR spectrum of 1.

Fig. S6 TG curve of 1.
Figure S7 The plot of $\chi_M^{-1}$ versus $T$ for 1.