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A series of new 3-D boratopolyoxovanadates based on different K-O-

K building blocks

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Fig. S1 Simulated and experimental powder XRD patterns of 1, 3, 4 and 5.



Fig. S2 Vanadium 2p XPS spectrum of 1.



Fig. S3 The coordination environment of K^+ ion in **2**.



Fig. S4 The coordination environment of K^+ ion in **3**.



Fig. S5 Structure of dimeric $[K_2O_{16}]$ unit in **5**.





Fig. S6 the solid-state reflectance spectra of 1 and 4.



Fig. S7 Plot of $\chi_M T$ vs T for 4.



Fig. S8 The IR spectra of 1-5.



Fig. S9 Thermogravimetric analyses curves of 5.

Thermogravimetric analysis of **5** was carried out in N₂ from 25 to 800 °C with a heating rate of 10 °C ·min⁻¹. A three-step weight loss occurs in the range of 25-700 °C which is related to the removal of free water molecules, coordinated water molecules, -OH groups and the H₃dien³⁺ ions (found, 27.0 %; calcd, 26.5 %).