

Fig. s1. The XPS spectrum for the compound 1. XPS measurements were performed on single crystals with ESCALAB MARK II apparatus, using the Mg K α (1253.6eV) achromatic X-ray radiation source.



Fig.s2. (a) The XPS spectrum for compound $\mathbf{2}$. (b) The XPS spectrum for compound $\mathbf{3}$.



fig. s3. The UV-Vis spectrum for the compound **1**. The UV-Vis spectra were recorded on a Shimadzu UV3100 spectrophotometer.



Fig.s4. The UV-Vis spectra for compound 1 and 2. Compound 1 and 2 were analysized as saturated N,N-dimethyl formamide solutions.



Fig. s5. The XRD pattern for compound 1. The X-ray powder diffraction pattern was obtained with a Scintag X1 powder diffractometer system using K α radiation with a variable divergent slit and a solid-state detector.



Fig. s6. (a) The XRD spectrum for compound 1. (b) The XRD spectrum for compound 2.



Fig. s7. (a) The IR spectrum for the compound **1**. The strong band at 1062cm⁻¹ is associated with the P centre of the POM in **1**. (b) The IR spectrum for the compound **2**.



Fig. s8. The TG curve for the compound **1**. Thermogravimetric analysis (TG) data were recorded with a thermal analysis instrument (SDT 2960, TA Instruments, New Castle, DE) with the heating rate of 10° C min⁻¹ in an air flow.



Fig. s9. (a) The TG spectrum for compound $\mathbf{2}$. (b) The TG spectrum for compound $\mathbf{3}$.

D-H···A	D-H[Å]	H…A[Å]	D…A[Å]	$D-H\cdots A[\circ]$	symop-for-A
C27A-H27AO9	0.93	<mark>2.39</mark>	3.18(2)	<mark>144</mark>	1-x,1-y,-z
C38A-H38AO15	0.93	<mark>2.49</mark>	3.15(2)	<mark>128</mark>	-x, 1-y, 1-z
C63A-H63A017	0.93	<mark>2.44</mark>	3.12(2)	<mark>129</mark>	x, -1+y, 1+z
C13A-H13A…Ow2	0.93	<mark>2.46</mark>	3.16(3)	<mark>131</mark>	1-x, 1-y, 1-z
O17…Ow1			2.76(4)		
OW1…Ow2A			2.80(5)		2-x, -y, 1-z
O17…Ow2			2.96(4)		

Table s1. The hydrogen bonds in compound **2**.