Electronic Supplementary Information (ESI)

A Ni-added polyoxometalate: synthesis, structure and catalytic performance

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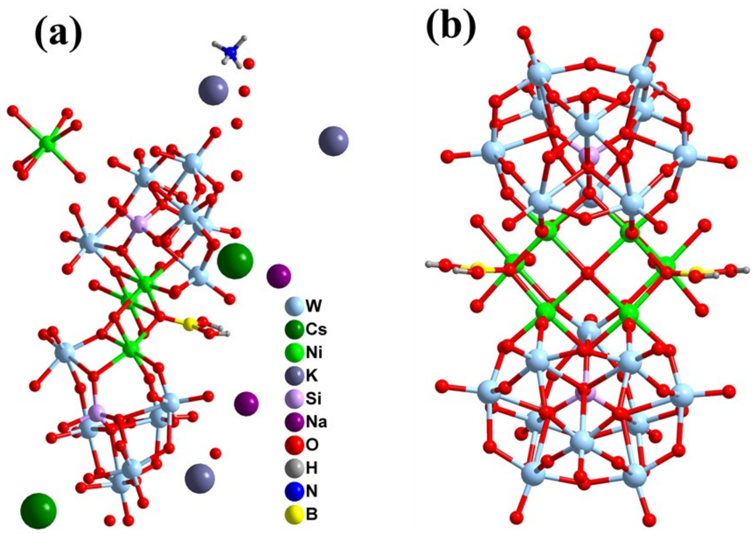

Fig. S1. (a) The asymmetric structural unit of **1**; (b) Ball an stick model diagram of **1a**.

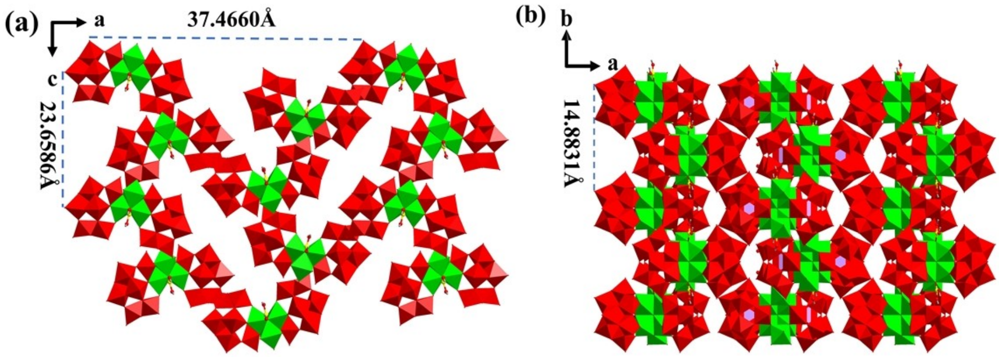

Fig. S2. (a) The packing mode of **1a** along the *b*-axis. (b) The packing mode of **1a** along the *c*-axis. Color labels for polyhedra: WO_6, red; SiO_4, purple; NiO_6, green.

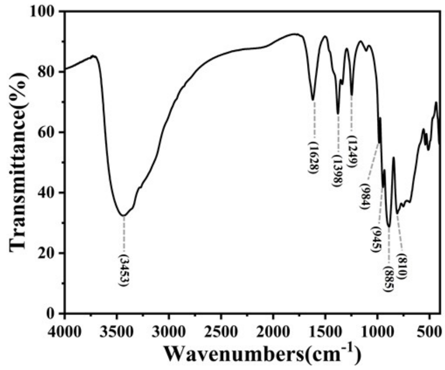

Fig. S3. The FT-IR spectrum of **1**.

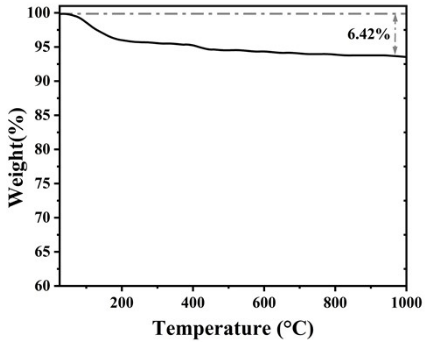

Fig. S4. TG curve of **1**.

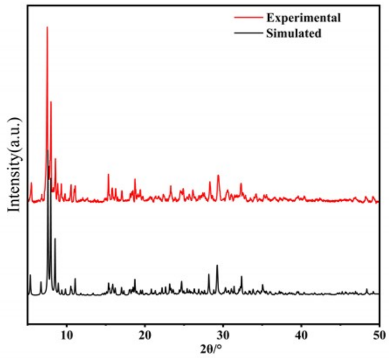

Fig. S5. Experimental and simulated PXRD patterns of **1**.

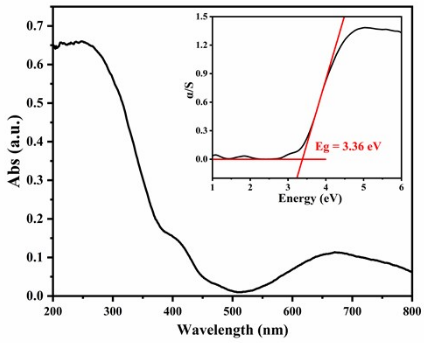

Fig. S6. UV-Vis diffuse reflectance spectrum of **1** and the corresponding α/S-Energy curve (inset).

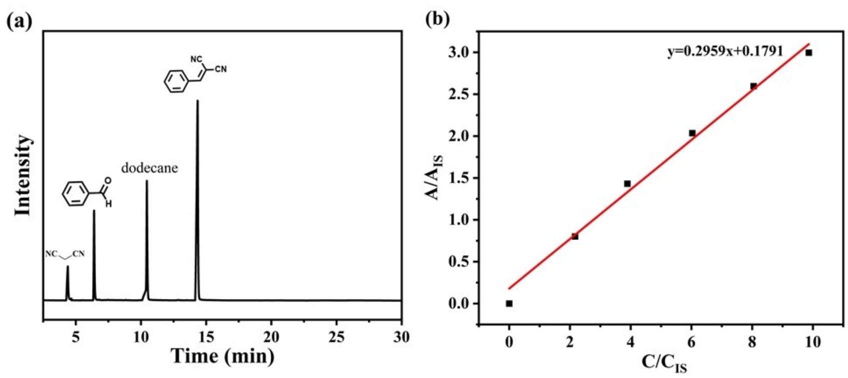

Fig. S7. (a) The Knoevenagel condensation of benzaldehyde with malononitrile detected by GC. Reaction conditions: 1 mmol benzaldehyde, 0.5 μmol catalyst, 1.2 mmol malononitrile, 3 mL CH_3OH, room temperature, 20 min. (b) Internal standard curve after fitting.

Table S1. BVS calculations of some atoms in **1**.

Atom	BVS	Atom	BVS
O3	0.328	O34	0.311
O13	2.020	O43	0.322
O20	2.117	O47	1.000
O22	2.044	O48	0.825
O30	1.064	B1	2.864

Table S2. Comparison of some POM-based catalysts for the Knoevenagel condensation reaction of benzaldehyde with malononitrile.

Compounds	Time (min)	Temp. (°C)	Conversion (%)	Ref.
$Na_8H[A\text{-}PW_9O_{34}]\cdot 7H_2O$	360	25	92	1
$Na_8H[B\text{-}PW_9O_{34}]\cdot 19H_2O$	360	25	89	1
$[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]^{4-}$	150	32	90	2
$[H(\gamma\text{-}SiW_{10}O_{32})_2(\mu\text{-}O)_4]^{7-}$	150	32	96	2
$Na_{16}[SiNb_{12}O_{40}]\cdot xH_2O$	120	25	100	3
$Mg_{0.73}Al_{0.22}(OH)_2[PW_{12}O_{40}]_{0.04}\cdot 0.98H_2O$	360	60	93	4
$K_7HNb_6O_{19}$	45	RT	99	5

$[H_2N(CH_3)_2]_2Na_{18}Cs_2H_{13}[(Cs_7(H_2O)_6)@\{(PO_4)@(Ni_4(OH)_3(WO_4))_3@(B\text{-}\alpha\text{-}PW_9O_{34})_3\}_2]\cdot30H_2O$	60	30	99	6
$[H_2N(CH_3)_2]_2Na_3H_5[\{Ti(C_2O_4)(H_2O)\}\{Ti(C_2O_4)\}(B\text{-}\beta\text{-}SbW_9O_{33})_2]\cdot22H_2O$	90	30	99	7
$K_2Na_{14}H_{10}[\{Ni_6(OH)_3(H_2O)_6(GeW_9O_{34})\}\{Ni_8(\mu_6\text{-}O)(OH)_3(H_2O)BO(OH)_2B_2O_3(OH)_2(GeW_9O_{34})_2\}]_2\cdot46H_2O$	90	30	100	8
$K_4Na_4H_{12}[(\{Ni_8(\mu_6\text{-}O)\}@\{B_4O_8(OH)_3\}_2)@(B\text{-}\alpha\text{-}GeW_9O_{34})_2]\cdot16H_2O$	90	30	100	9
1	50	RT	100	This paper

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