Electronic Supplementary Material (ESI) for Dalton Transactions.

A Zr-added Dawson-type poly(polyoxometalate)

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Table S1 The crystallographic data and structure refinement for **1**.

	1
Empirical formula	$C_{20}H_{108}N_{10}O_{190}P_6W_{48}Zr_6$
Formula weight	13087.11
Crystal system	Triclinic
Space group	*P*-1
a, Å	23.2407(17)
b, Å	23.246(2)
c, Å	29.7083(16)
α, deg	108.197(7)
β, deg	94.803(5)
γ, deg	117.841(9)
V, $Å^{-3}$	12969.2(17)
Z	2
μ, mm^{-1}	21.539
F(000)	11400
T, K	293(2)
Limiting indices	$-27 \leq h \leq 27$ $-27 \leq k \leq 26$ $-35 \leq l \leq 35$
No. of reflections collected	107349
No. of independent reflections	45590
R_{int}	0.0876
Data / restrains / parameters	45590 / 129 / 2486
GOF on F^2	0.972
Final *R* indices [$I>2\sigma(I)$]	$R_1 = 0.0738$ $wR_2 = 0.1582$
R indices (all data)	$R_1 = 0.1500$ $wR_2 = 0.1904$
Largest diff. peak and hole,e·$Å^{-3}$	3.820, −2.835

Physical measurements. The precursor of $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 24H_2O$ was made as previously described[1] and further identified by IR spectra. All other chemicals were commercially purchased without further purification and disposal. IR spectra were recorded with a Smart Omni-Transmission spectrometer using KBr pellets in the range of 400–4000 cm^{-1}. Powder X-ray diffraction (PXRD) pattern was obtained by using a Bruker D8 Advance XRD diffractometer with Cu Kα radiation (λ = 1.54056 Å). Thermogravimetric (TG) test was performed under a N_2 atmosphere on a Mettler–Toledo TGA/SDTA 851e instrument with a heating rate of 10 °C min^{-1} from 25 to 800 °C. The GC spectra were obtained on a SHIMADZU GC-2014C.

1. R. G. Finke, M. W. Droege and P. J. Domaille, *Inorg.Chem.,* 1987, **26**, 3886–3896.

X-ray crystallography. Intensity data for **1** was collected on a Gemini A Ultra diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K. The structure was solved by the direct method and refined on F^2 by full-matrix least-squares methods using the SHELX 97 program package.[2] No hydrogen atoms associated with water molecules were located from the difference Fourier map. In the structural refinements, the "omit" constraint was used owing to the low-quality diffraction data in high θ. In order to balance the charge of compound **1**, 14 protons should be added. The crystallographic data and structure refinement parameter for **1** are listed in Table S1.

2. (a) G. M. Sheldrick, *SHELXS97: Program for Crystal Structure Solution*, University of Göttingen: Göttingen, Germany, 1997; (b) G. M. Sheldrick, *SHELXL97: Program for Crystal Structure Refinement*, University of Göttingen: Göttingen, Germany, 1997.

Synthesis of $[H_2N(CH_3)_2]_{10}H_{14}[(Zr_2P_2W_{16}O_{61})_3]\cdot 7H_2O$ (1). $K_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 24H_2O$ (1.004 g, 0.227 mmol), $ZrOCl_2\cdot 8\text{-}H_2O$ (0.154 g, 0.478 mmol), Li_2CO_3 (0.300 g, 4.060 mmol) and dimethylamine hydrochloride (0.521 g, 6.390 mmol) were added to 30 mL of LiOAc-HOAc (0.5 $mol\cdot L^{-1}$). After vigorous stirring for 20 min, the pH of the solution was about 5.0. Then the resulting solution was sealed in a 100 mL Teflon-lined bomb and heated at 100 °C for 1 days. After cooling to ambient temperature, colorless block crystals of **1** were obtained. Yield: 74 mg (7.47% based on $K_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 24H_2O$). IR (KBr, cm^{-1}): 3430 (s), 3160 (m), 2789 (w), 1627 (m), 1463 (m), 1084 (vs), 954 (s), 897 (s), 779 (vs).

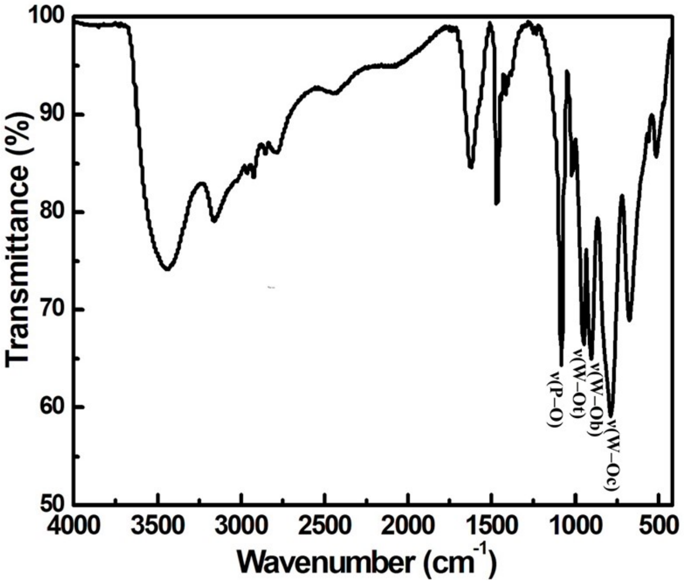


Fig. S1 The IR spectrum of **1**.

IR spectrum. The IR spectrum of **1** has been recorded in the range of 4000–400 cm^{-1} (Fig. S1). Four absorption peaks appearing at 1084, 954, 897 and 779 cm^{-1} are respectively assigned to the characteristic vibrations of $v_{(\mathrm{P–O})}$, $v_{(\mathrm{W–Ot})}$, $v_{(\mathrm{W–Ob})}$ and $v_{(\mathrm{W–Oc})}$. In the high wavenumber region, the occurrence of a wide band at 3430 cm^{-1} and an intense band centered at 1626 cm^{-1} belongs to the stretching and bending vibrations of O–H. Three weak bands appearing at 3160 cm^{-1}, 2789 cm^{-1} and 1463 cm^{-1} are respectively assigned to the N–H, C–H and C–N stretching vibrations, indicating the presence of $[H_2N(CH_3)_2]^+$.

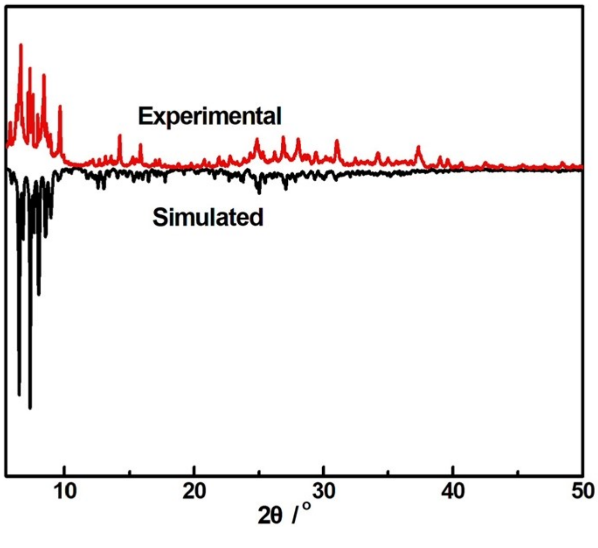


Fig. S2 The experimental and simulated PXRD patterns of **1**.

PXRD. The phase purity of 1 was determined by the good consistency between the simulated and experimental PXRD patterns (Fig. S2). The difference in intensity between the experimental and simulated PXRD patterns may be due to the change in the preferred orientation of the powder samples during the acquisition of the experimental PXRD patterns.

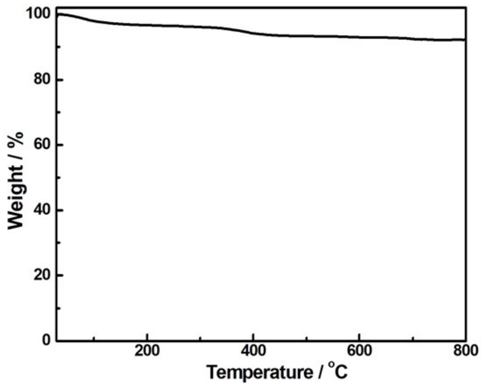


Fig. S3 The TG curve of **1**.

Thermogravimetric analysis. The TG has been measured on sample under flowing N_2 atmosphere in the temperature range of 25–800 °C. As shown in Fig. S3, it is easy to find that there is two-step of weight loss in the TG curve. The first step weight loss of 3.41 % (calcd. 3.36 %) takes place between 25 and 200 °C attributed to the loss of 7 lattice water and 18 adsorbed water molecules. The second step weight loss of 4.87 % (calcd. 4.97 %) occurs in the temperature range of 200–800 °C ascribed to the removal of 10 dimethylamine groups and the dehydration of 24 protons. The total weight loss is 8.28% (calcd. 8.33 %) for **1**. Obviously, the TG result is basically consistent with the structural determination.

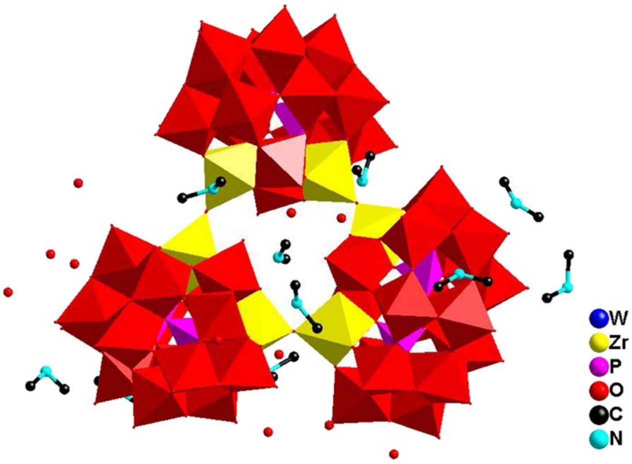
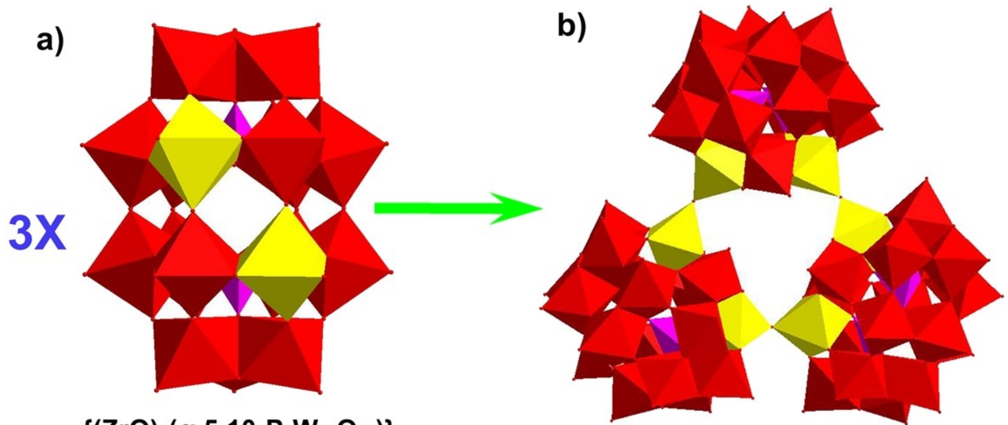


Fig. S4 The asymmetric unit of **1**.



{(ZrO)$_2$(*α*-5,10-$P_2W_{12}O_{60}$)}

Fig. S5 (a) The (ZrO)$_2$(*α*-5, 10-$P_2W_{16}O_{60}$) subunit; (b) The polyoxoanion **1a**.

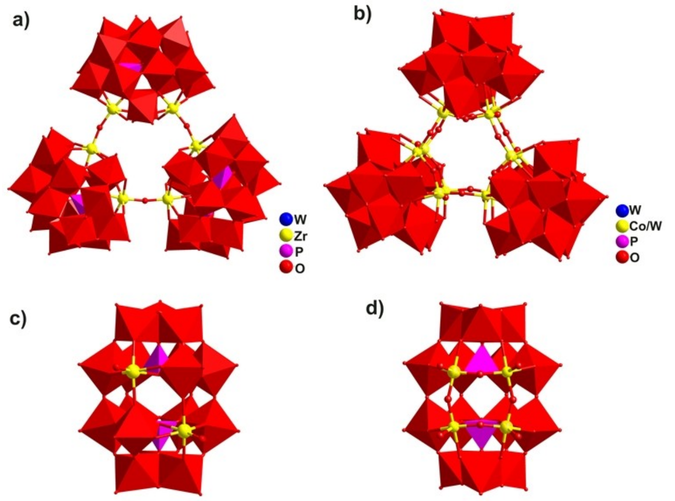


Fig. S6 (a) The polyoxoanion **1a;** (b) The $[(Co_2P_2W_{16}O_{60})_3]^{24-}$ cluster; (c) The $(ZrO)_2(\alpha\text{-}5,10\text{-}P_2W_{16}O_{60})$ subunit; (d) The $Co_2P_2W_{16}O_{62}$ subunit.

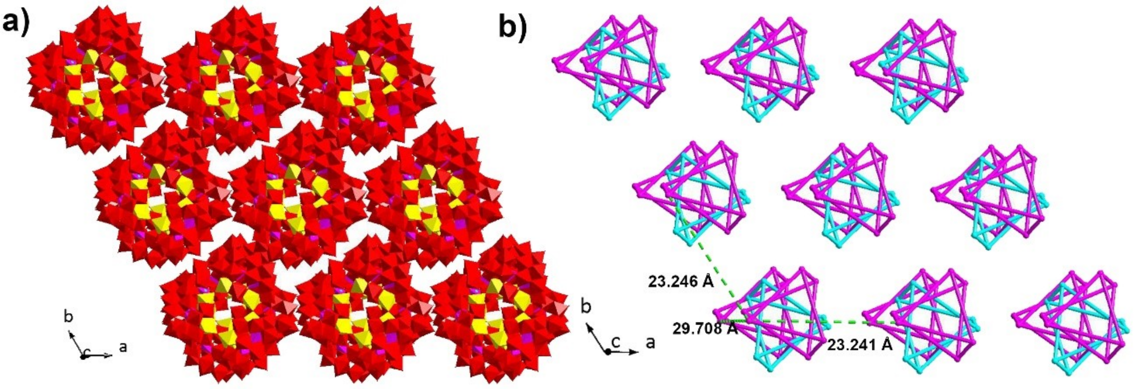


Fig. S7 (a) and (b) View of the stacking and the simplified packing of **1a** viewed along the c axis.

It can be found from 3D stacking diagram and the simplified packing that **1a** present a regular arrangement of –AAA– along the *a* and *b* axes with distances of 23.421 and 23.426 Å, respectively, and array in the fashion of –ABA– along the *c* axis with distance of 29.708 Å (Fig. S7).

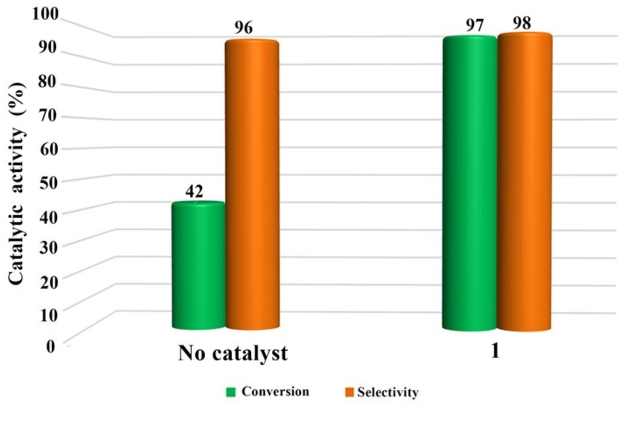


Fig. S8 The comparative experiments under the same reaction conditions.

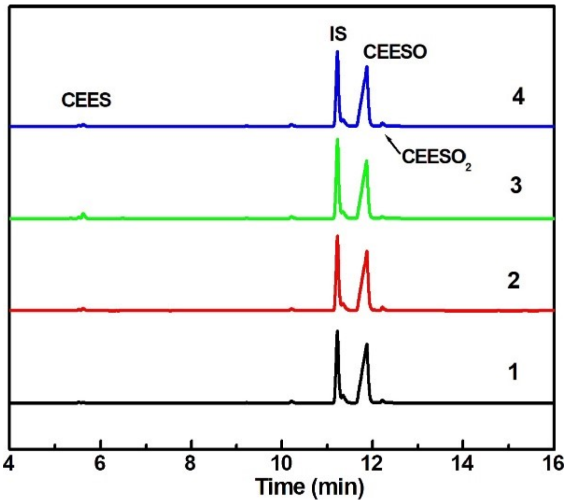


Fig. S9 GC-FID signals for the recycling experiments of the catalytic oxidation.

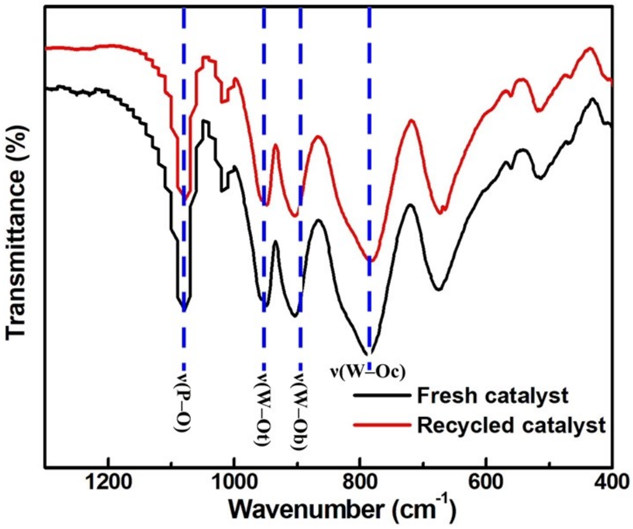


Fig. S10 IR spectra of the fresh and the recycled catalyst **1**.

As is shown in Fig. S10, the four characteristic peaks of POM skeleton, ν(P-O), ν(W-Ot), ν(W-Ob) and ν(W-Oc), in the IR spectrum of recycled catalyst are well consistent with those in the IR spectrum of fresh catalyst, indicating that the catalyst structure is stable in the catalytic process.