Supporting Information

Two new hexa-Ni-substituted polyoxometalates from isolated cluster to 1-D chain: syntheses, structures, and properties

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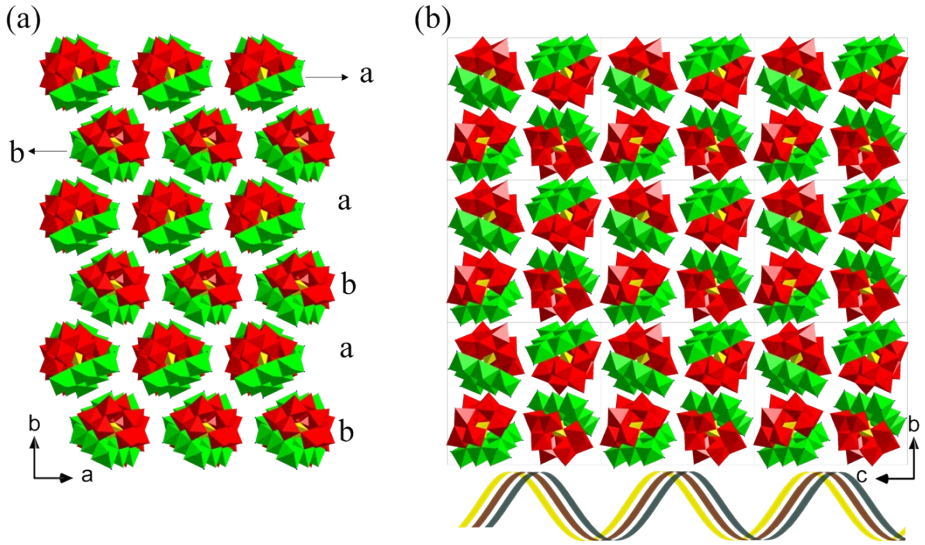

Figure S1 Three-dimensional stacking diagram of compound **1** along the *c*-axis (a) and the *a*-axis (b).

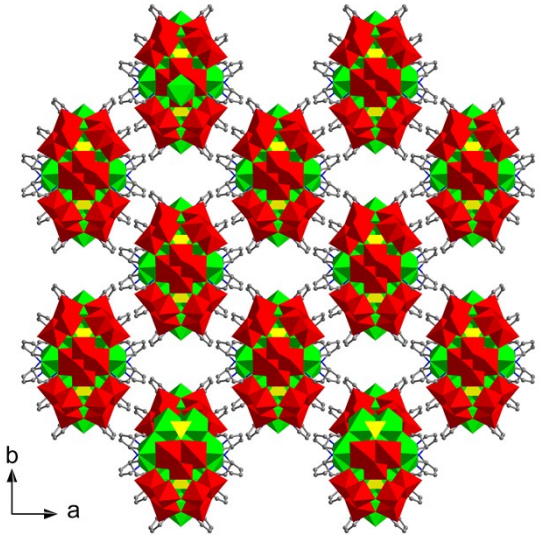

Figure S2 Three-dimensional stacking diagram of compound **2** along the *c*-axis

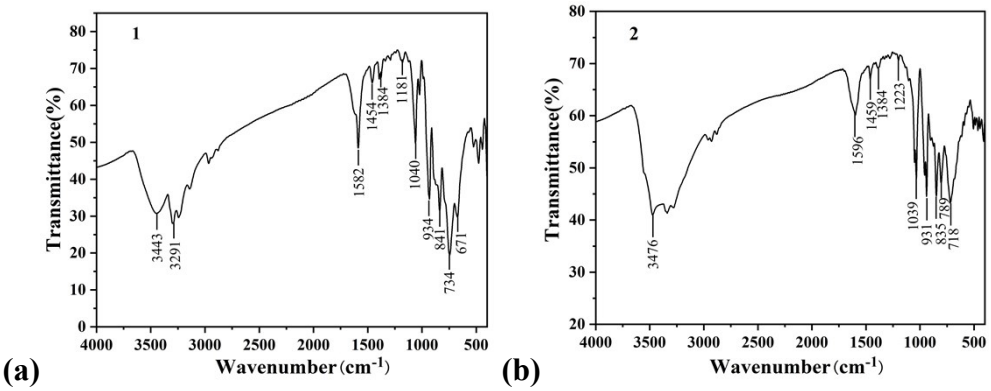

Figure S3 The IR spectra of compounds **1**–**2**.

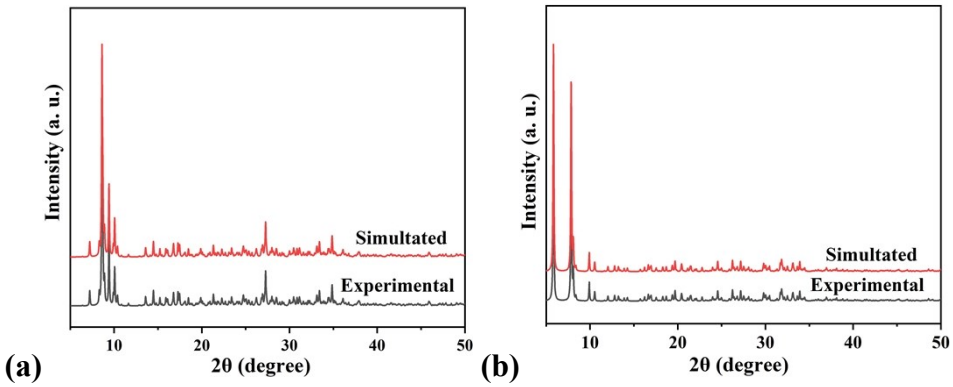

Figure S4 Powder X-ray diffraction patterns of compounds **1**-**2**.

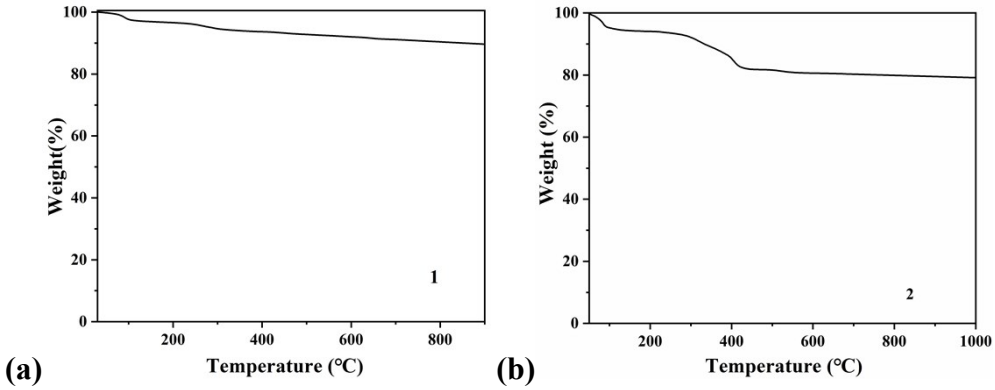

Figure S5 The TG curves of compounds **1**-**2**.

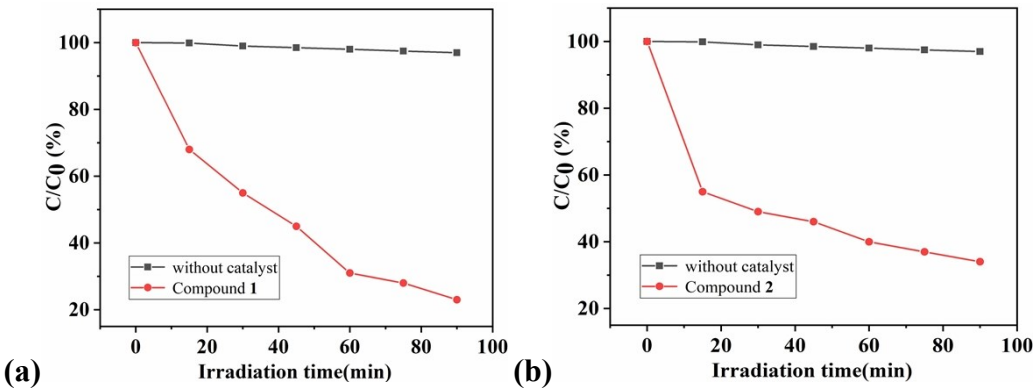

Figure S6 Photocatalytic decomposition rate of MB solution under UV (a) **1** and (b) **2**.

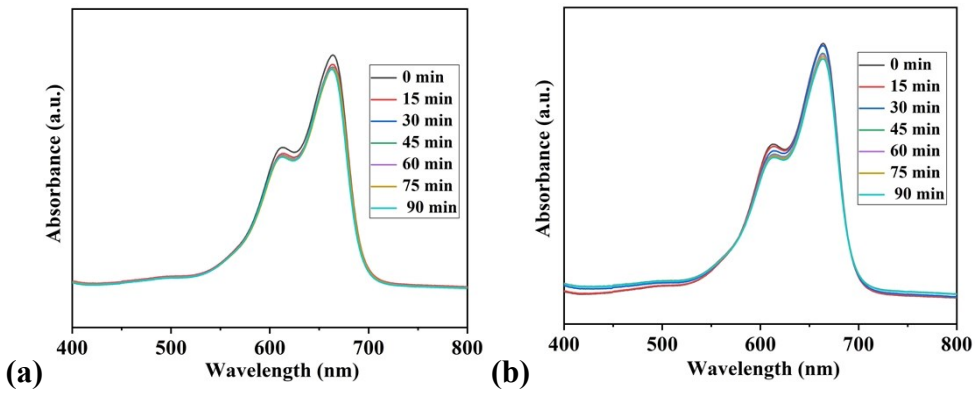

Figure S7 Photocatalytic decomposition rate of MB solution under dark room (a) **1** and (b) **2**.

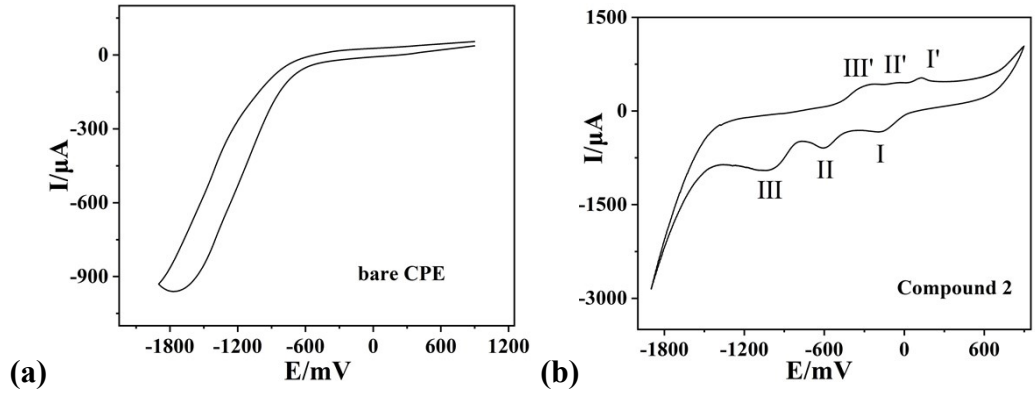

Figure S8 (a) Cyclic voltammograms of the bare CPE and (b) **2**–CPE in 0.5 M H_2SO_4/Na_2SO_4 solutions (pH = 4.8) aqueous solution at 300mV·s^{-1}

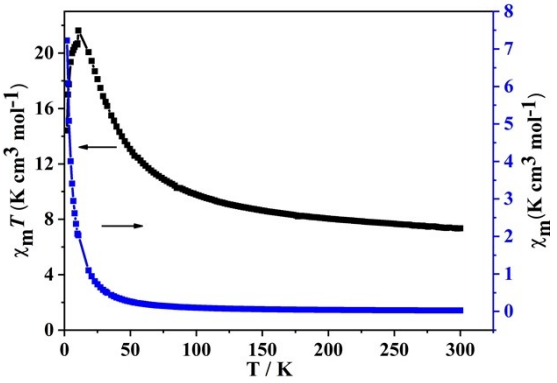

Figure S9 Temperature dependence of χ_m and $\chi_m T$ values for **1**.

Since compounds **1-2** contain $\{Ni_6PW_9\}$ SBUs, we only take compound **1** as an example to analyze its magnetic properties. The magnetic susceptibility of **1** was measured at 2-300 K (Fig. S9). The experimental χ_m values at 300 K and 50 K were 1.12 emu mol^{-1} and 1.61 emu mol^{-1}, displaying a slight increasing trend. Upon cooling, χ_m acutely increased to reach 7.485 emu mol^{-1} at 2 K. the value of $\chi_m T$ increased from 7.437 emu mol^{-1} K at 300 K per formula unit, and it reach a maximum of 21.925 emu mol^{-1} at 13 K and then it suddenly decreased below 13 K, which might be ascribed to the existence of zero-field splitting. This behavior of $\chi_m T$ for **1** showed the presence of overall ferromagnetic coupling interactions with S = 6 spin ground state for the hexa-Ni^{II} cluster in **1**.

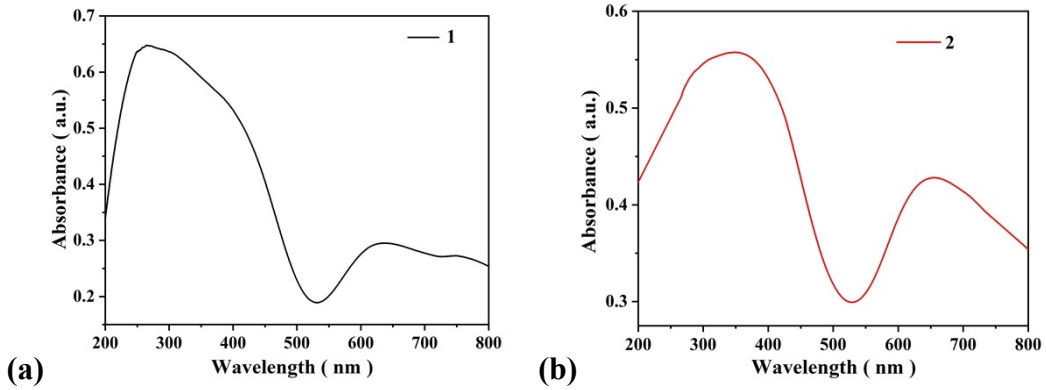

Figure S10 The electronic absorption spectrum of compounds **1**-**2** in the crystalline state.

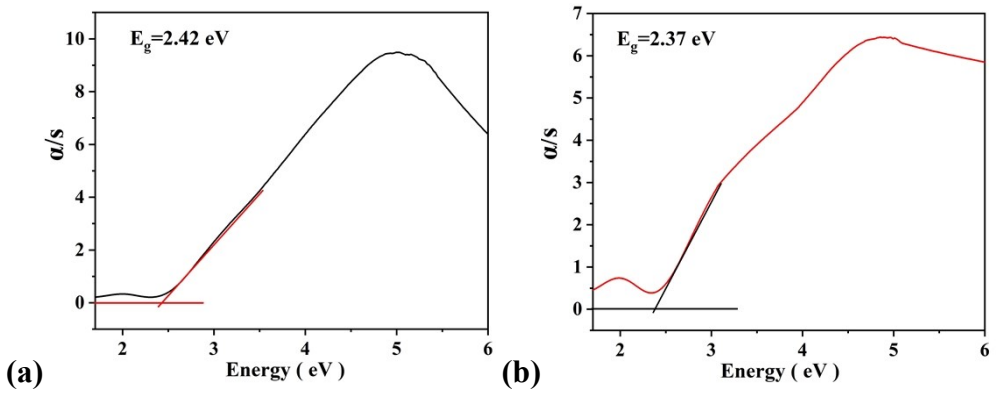

Figure S11 Diffuse reflection spectra of Kubelka−Munk (K-M) function versus energy (eV) of compound **1(a)**−**2(b)**.

Optical Band Gaps

To evaluate the semiconductor behaviors and photocatalytic activities of compounds **1**−**2**, the diffuse reflection spectra of compounds **1**−**2** were carried out in the crystalline state at room temperature (Fig. S10). The band gaps (Eg) of compounds **1**−**2** were obtained from the Kubelka−Munk (K-M) function F vs E,[1] which are estimated to be 2.42 eV for **1** and 2.37 eV for **2**, respectively (Fig. S11). The band gap values indicate that compounds **1**−**2** may respond to UV irradiation and have the potential capacity for photocatalytic reactions.[2]

1 Pankove, J. I. Optical Processes in Semiconductors; Prentice−Hall, Inc.: Englewood Cliffs, NJ, 1971; 34.

2 (a) T. Wen, D. X. Zhang and J. Zhang, Inorg. Chem., 2013, **52**, 12; (b) M. C. Das, H. Xu, Z. Y. Wang, G. Srinivas, W. Zhou, Y. F. Yue, V. N. Nesterov, G. D. Qian and B. L. Chen, Chem. Commun., 2011, **47**, 11715; (c) W. Q. Kan, B. Liu, J. Yang, Y. Y. Liu and J. F. Ma, Cryst. Growth Des., 2012, **12**, 2288.