

Multi-functional optical properties of a cesium-octacyanotungstate

(Graduate School of Science, University of Tokyo) ○Tatsuya Konishi, Kunal Kumer, Yuuki Mineo, Kazuki Nakamura, Taiki Sakaguchi, Koji Nakabayashi, Shin-ichi Ohkoshi

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Molecular-based magnets that exhibit various optical properties can be controlled by selecting certain ligands and central metal ions. In our laboratory, we have constructed multifunctional complexes such as polar crystals with switchable superionic conduction and ferromagnets including controllable luminescence properties by excitation light.^{1,2} Herein we report a functional complex of $\text{Cs}_3[\text{W}(\text{CN})_8](\text{glycine})$ exhibiting second harmonic generation (SHG), luminescence, THz-wave absorption, and antiferromagnetic magnetic ordering.

Orange crystals were obtained by mixing an aqueous solution of $\text{Cs}_3[\text{W}(\text{CN})_8] \cdot 2\text{H}_2\text{O}$ and glycine, filtrating, and leaving to stand some hours. Single crystal X-ray diffraction analysis revealed that the compound belonged to a tetragonal crystal system with a non-centrosymmetric space group of $P4bm$, resulting in SHG (Figure 1). The complex shows SH light and red luminescence at the same time by irradiation with 1040 nm laser. The result of UV-vis spectrum and emission spectrum shows that the compound absorbed 520 nm light and emitted 772 nm red light luminescence derived from a $[\text{W}^{\text{V}}(\text{CN})_8]^{3-}$ moiety (Figure 2). Moreover, THz-TDS measurements showed broad absorption peaks near 1 THz which were assigned to low frequency phonon modes. In addition, the title complex exhibits an antiferromagnetic ordering around 25 K due to antiferromagnetic couplings among spins of the $[\text{W}^{\text{V}}(\text{CN})_8]^{3-}$ sites ($S = 1/2$).

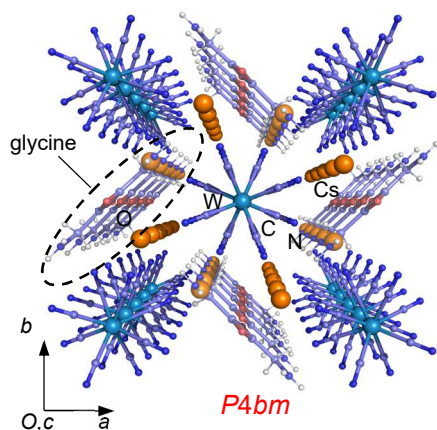


Figure 1 Crystal structure of $\text{Cs}_3[\text{W}(\text{CN})_8](\text{glycine})$ viewed from the c -axis.

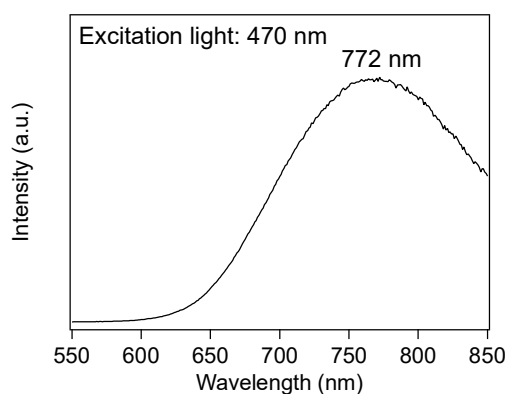


Figure 2 Emission spectra of $\text{Cs}_3[\text{W}(\text{CN})_8](\text{glycine})$ at 298 K.

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