A pentacyanidonitrosylmetallate-based assembly exhibiting switchable nonlinear optical functionalities

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Noncentrosymmetric materials are extensively studied due to their unique optical properties and we have investigated noncentrosymmetric cyanido-bridged bimetal assemblies with second harmonic generation (SHG).[1,2] In this work, we prepared a Dy-$[Fe(CN)_5(NO)]$ one-dimensional metal assembly, $[Dy(phen)_2(NO_3)(H_2O)][Fe(CN)_5(NO)]\cdot 3H_2O$ (phen = 1,10-phenanthroline), and investigated the crystal structure, physical and nonlinear optical features, and their photoswitching effect.[3]

The target compound was obtained by reacting an aqueous solution of $Na_2[Fe(CN)_5(NO)]$ and $Dy(NO_3)_3$ with a methanolic solution of phen, and possesses an orthorhombic structure with a polar $Pna2_1$ space group composed of a cyanide bridged one dimensional chain structure (Figure 1a). The NO ligands direct along the crystallographic *c*-axis, resulting in spontaneous electric polarization along *c*-axis. The UV-vis spectrum contains metal-to-ligand charge transfer (MLCT) bands from 3d orbitals of Fe to π^* orbitals of NO, and f–f transitions of Dy^{III}. SHG measurements of a single crystal using a femtosecond pulsed laser (wavelength: 1040 nm) showed that the detected 520-nm light intensity is quadratically proportional to the fundamental light power, supporting that the observed signal is due to SHG. The analyzer angle versus SH intensity shows that the output SH light is polarized along the crystallographic *c*-axis direction, and the SH intensity increased 5 times as large as the intensity before irradiation by irradiating 473-nm laser at 100 K. Successive irradiating with 804-nm light reduces the SH intensity. The observed photoswitching of SHG is caused by the photoinduced linkage isomerization of the iron nitrosyl sites, i.e., Fe–NO ↔ Fe–ON, confirmed by the photoirradiation experiment of IR spectrum.

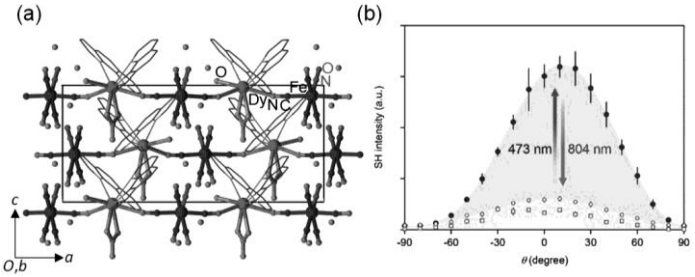

Figure 1. (a) Crystal structure viewed from *b*-axis. (b) The analyzer angle versus SH intensity before irradiation (open circles), after 473-nm irradiation (closed circles), and after 804-nm irradiation (open squares).

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