Supplementary Materials for:

Hybrid Microtubes of Polyoxometalate and Fluorescence Dye with Tunable Photoluminescence

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1. Chemicals and measurements

HCl and fluorescein sodium (FS) were used as received. Monolacunary tungstosilicate α-$K_8[SiW_{11}O_{39}]$ (α-SiW_{11}) was synthesized according to the published procedure.[1] All reagents were used as received without further purification. All the aqueous solutions were prepared using de-ionized water.

Elemental analyses were carried out on a Euro Vector EA 3000 and Vario EL instruments. SEM images were taken with a XL30 field emission environmental scanning electron microscope (ESEM-FEG). FT-IR spectra were measured on a D/MAX-IIIC spectrometer. Powder XRD patterns were recorded with a D/max-IIIC diffractometer. Thermogravimetric analysis measurements (TG) were performed with a Perkin-Elmer TGA7 instrument. UV/Vis spectra were captured on 756 CRT and Cary 500 UV-Vis-NIR spectrophotometer. Fluorescence spectra were measured on an FLSP920 Edinburgh Fluorescence Spectrometer. The fluorescent stability was

performed with a HITACHI F-7000 fluorescence spectrophotometer. Fluorescence microscopy images were obtained with an Olympus FV-1000 confocal laser scanning microscope with mercury lamp as excitation source, using CCD scanning (objective lens 20 times).

2. Control experiment for chemically synthesized SiW_{12}-F and physically dyed SiW_{12}/F microtubes

To make a comparison between the chemically synthesized SiW_{12}-F microtubes and the physically dyed SiW_{12}/F microtubes, a control experiment was designed. Pre-synthesized SiW_{12} microtubes [2] were dipped into a fluorescein sodium solution of pH=1, then dried in air to obtain physically dyed (SiW_{12}/F) microtubes. The microscope images of the products show that the color of SiW_{12}-F microtubes is well spread, but SiW_{12}/F microtubes are not dyed evenly (**Fig. S1**). These facts reveal that F dye is doped into the crystal structure of the SiW_{12} microtubes during chemical synthesis of SiW_{12}-F microtubes.

Fig. S1. Microscope images for (top) chemically synthesized SiW_{12}-F and (bottom) physically dyed SiW_{12}/F microtubes.

3. Preparation of other fluorescent microtubes

The preparation of other fluorescent microtubes is as for the procedure for SiW_{12}-F microtubes except for variation of fluorescent dyes: Fluorescent Green 4A (0.0160 g); Fluorescent Red XD (0.056 g); Fluorescent Violet XD (0.0040 g); Fluorescein GG (0.0114 g); Fluorescent Green 10G (0.0020 g); Methyl violet ethanol solution (2 mL of 7.1×10^{-4} M); Invisible Fluorescent Blue (0.0400 g) and Fluorescent Blue XD (0.0190 g). Optical micrograph images of the products are shown in **Fig. S3.**

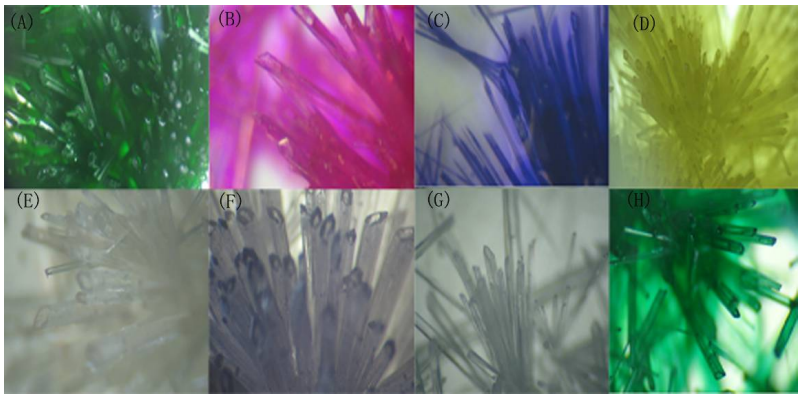

Fig. S2. Optical micrograph images of the other fluorescent microtubes: (A) Fluorescent Green 4A; (B) Fluorescent Red XD; (C) Fluorescent Violet XD; (D) Fluorescein GG; (E) Fluorescent Green 10G; (F) Methyl Violet; (G) Invisible Fluorescent Blue; (H) Fluorescent Blue XD.

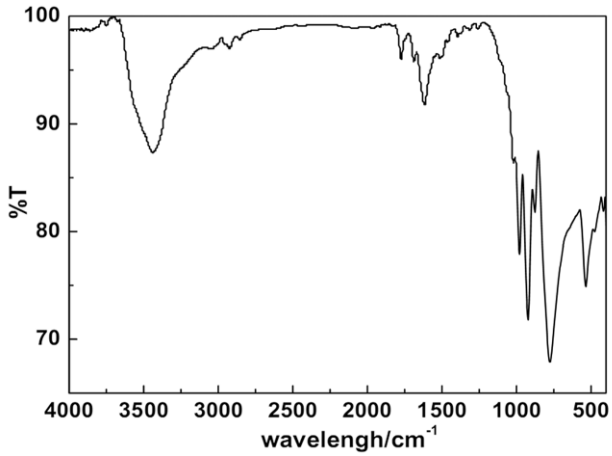

Fig. S3. FT-IR spectrum obtained from SiW_{12}-F microtubes.

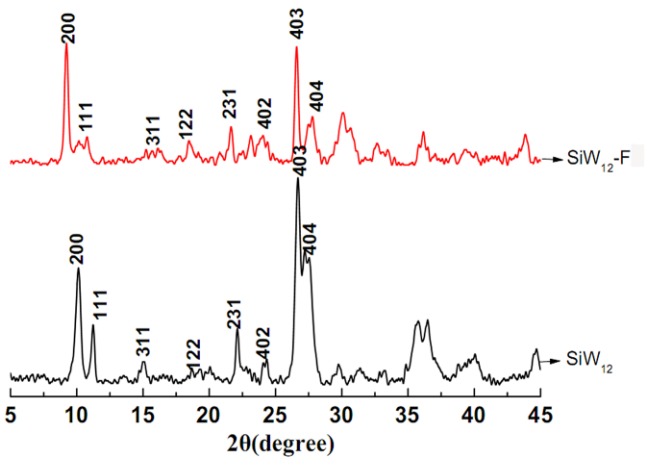

Fig. S4. XRD spectra obtained from SiW_{12}-F and SiW_{12} microtubes.

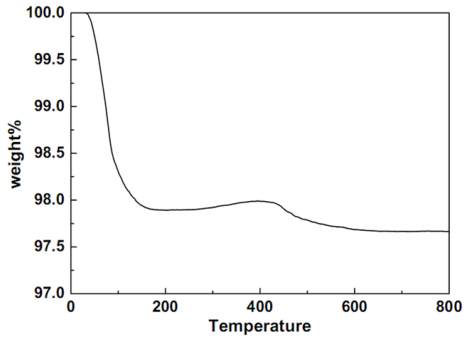

Fig. S5. TG curve obtained from SiW_{12}-F microtubes.

The TG measurement of SiW_{12}-F microtubes shows the initial weight loss of 2.09 % from 30-150 ºC, corresponding to the loss of four water molecules. The final weight loss of 0.246 % in the region of 420-500 ºC indicates the removal of organic F moiety. Weight loss calculations give an empirical ratio SiW_{12} : F of 1: 0.02, consistent with the element analysis results.

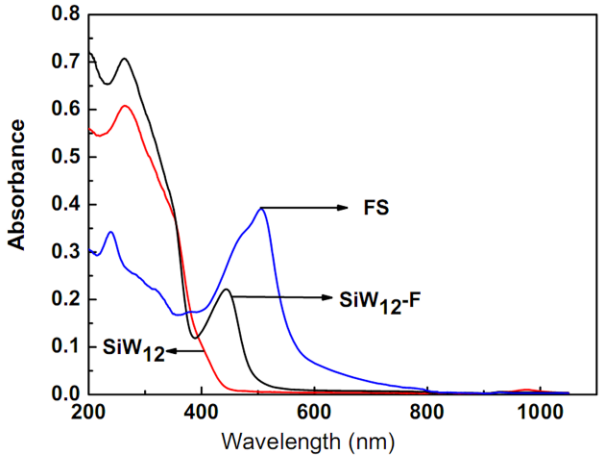

Fig. S6. Solid UV-Vis spectra obtained from FS powder, SiW_{12}-F and SiW_{12} microtubes.

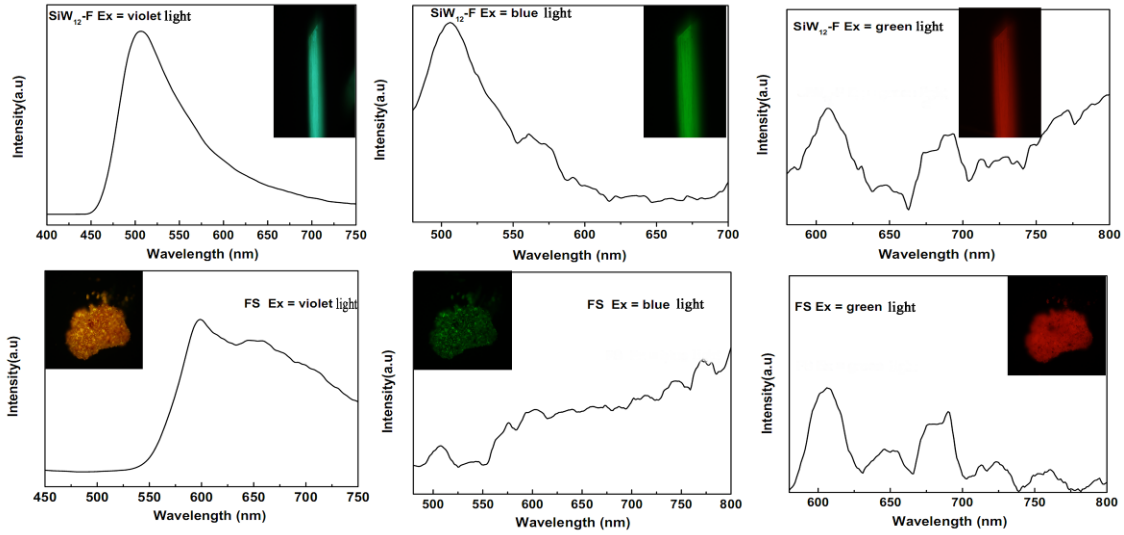

Fig. S7. Solid-state fluorescence emission spectra obtained from the SiW_{12}-F microtubes at room temperature by variation of excitation light (Ex), at 380 nm corresponding to violet light; at 458 nm corresponding to blue light; at 550 nm corresponding to green light. The insets are the fluorescence microscopy images of an individual SiW_{12}-F microtube (up) and FS powder (bottom). The light source is violet, blue and green light from left to right, respectively.

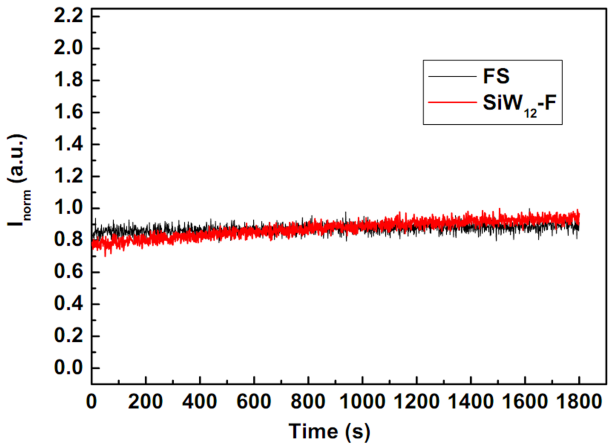

Fig. S8. Time-scan fluorescence spectra obtained from SiW_{12}-F microtubes (excitation at 380 nm, emission at 508 nm) and FS (excitation at 350 nm, emission at 650 nm for FS).

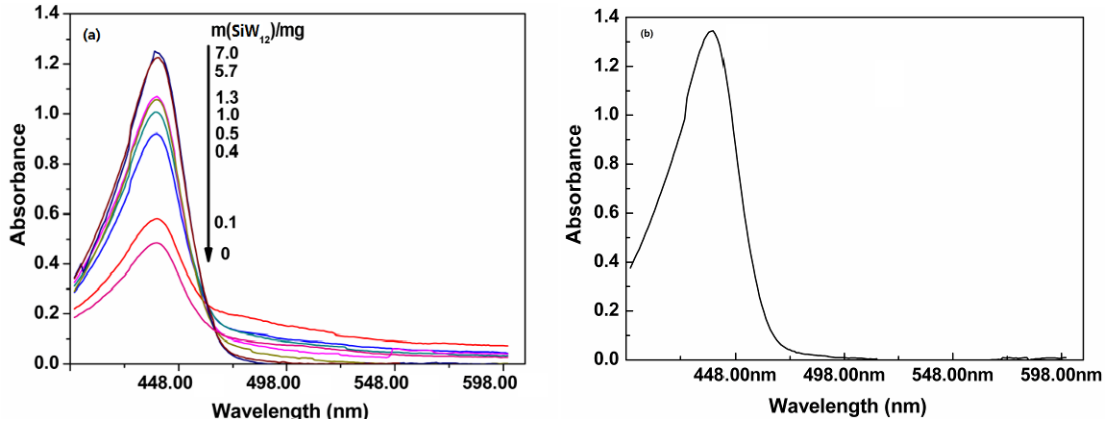

Fig. S9. Visble absorption spectra obtained from a 3 mL solution containing 1.33×10^{-5} molmL^{-1} FS (pH=1): (a) under the irritation by daylight for 8h in the presence of SiW_{12} (up to down: SiW_{12}= 7.0 mg, 5.7 mg, 1.3 mg, 1.0 mg, 0.5 mg, 0.4 mg, 0.1 mg and 0 mg; (b) in the dark (SiW_{12}= 0 mg). The m(SiW_{12}) means the mass of SiW_{12} microtubes.

[1] C. Rocchiccioli-Deltcheff, M. Fournier, R. Franck and R. Thouvenot., *Inorg. Chem.*, 1983, **22**, 207.

[2] Z. F. Xin, J. Peng, T. Wang, B. Xue, Y. M. Kong, L. Li and E. B. Wang, *Inorg. Chem.*, 2006, **45**, 8856.