

## Supplementary Information:

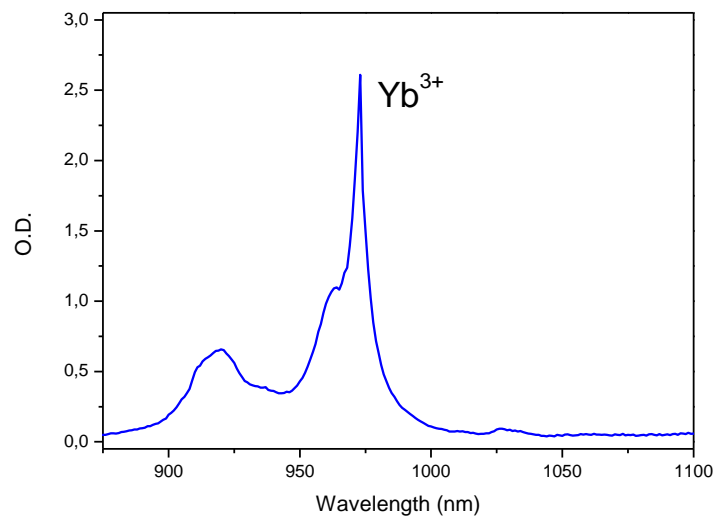
### Additional experimental details section

#### *About preparation of up-conversion samples*

Orthorhombic  $\text{K}_2\text{YbF}_5$  crystals containing  $\text{Tm}^{3+}$  ions were obtained under hydrothermal conditions.<sup>16</sup> In detail, fluoride crystals were synthesized by a direct temperature gradient method as a result of the reaction of the aqueous solutions containing 35–40 mol% KF with appropriate oxide mixtures  $(1-x)\text{Yb}_2\text{O}_3-x\text{Tm}_2\text{O}_3$  at a temperature of about 750 K, a temperature gradient along the reactor body of up to  $1 \text{ K cm}^{-1}$ , and a pressure of about 100 MPa.<sup>22</sup>

Under these conditions, spontaneously nucleated crystals from 0.1 to  $1.0 \text{ mm}^3$  in size were obtained for 75 h. Synthesized  $\text{K}_2\text{YbF}_5$  crystals were of long prismatic habit with the width/length ratio being about 1/10, which was caused by the chain structure of  $\text{K}_2\text{YbF}_5$ . The purities of the starting materials were higher than 99.99% for rare-earth oxides and 99.9% for KF. The structure type and phase purity of synthesized samples were characterized with conventional powder X-ray diffraction (XRD) technique and powder XRD patterns were obtained by using a Bruker D8 Advance X-Ray powder diffractometer with Cu K $\alpha$  radiation. Within this research crystals of  $\text{K}_2\text{YbF}_5$  doped with 0.2 at%  $\text{Tm}^{3+}$  were studied.

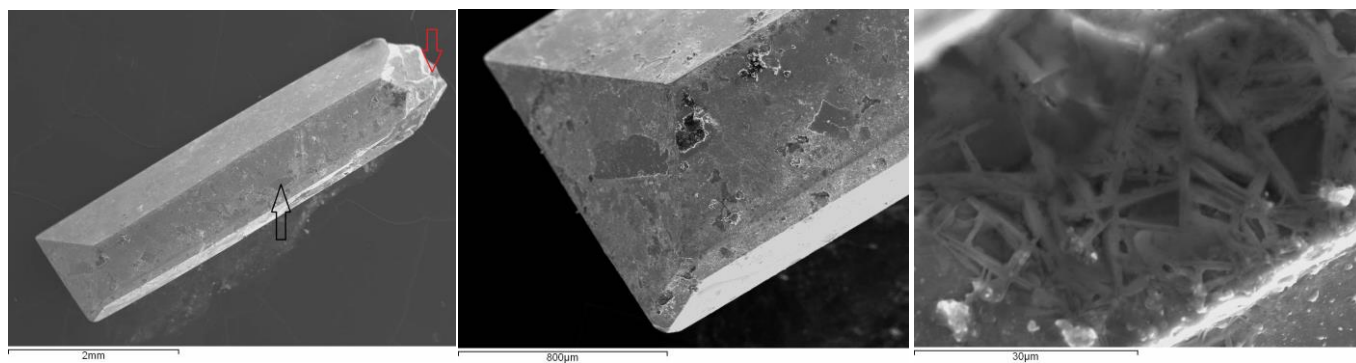
Fig. S1 shows an absorption spectrum of a hydrothermal 0.2 at %  $\text{Tm}^{3+}$  doped  $\text{K}_2\text{YbF}_5$  crystal measured by an UV-VIS-NIR spectrophotometer Perkin-Elmer Lambda 9 with a resolution of 0.5 nm. It can be clearly seen that there is an intense absorption peak corresponding to the  $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$  transition in  $\text{Yb}^{3+}$  ions at around 980 nm, which are resonant with many commercial NIR continuous-wave laser diodes, specifically with the ones used in our up-conversion driven photocatalytic experiments. On the other hand, due to the high absolute concentration of  $\text{Yb}^{3+}$  ions in  $\text{K}_2\text{YbF}_5$ , namely about  $8 \times 10^{21} \text{ at/cm}^3$ , and low concentration quenching, the totality of  $\text{Yb}^{3+}$  ions acts as an efficient collector of NIR photons the energy of which is transferred to an insignificant number of  $\text{Tm}^{3+}$  ions, less than  $1.6 \times 10^{19}$ , by energy migration over the  $\text{Yb}^{3+}$ -sublattice.



**Fig. S1.** Absorption spectra of a hydrothermal 0.2 at%  $\text{Tm}^{3+}$  doped  $\text{K}_2\text{YbF}_5$  crystal.

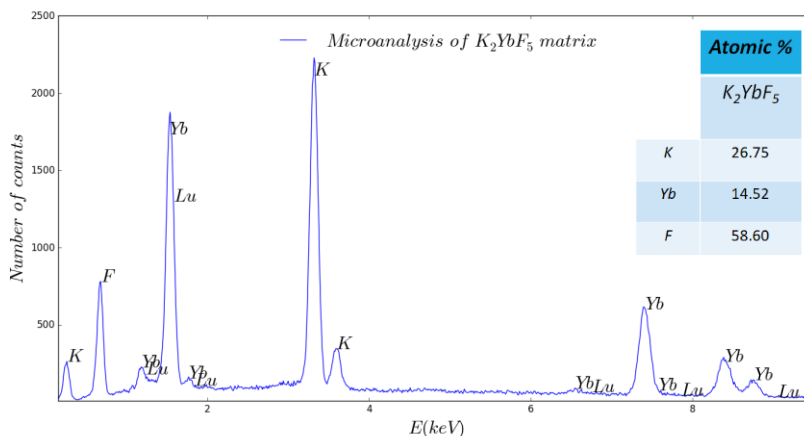
We have also made the morphological characterization of the UC  $\text{K}_2\text{YbF}_5$  crystal by means of SEM images. X-Ray micro-analyser of dispersive energies (EDX) microanalysis has been performed to obtain the elemental distribution by using a JEOL JSM 6300 electron microscope with a resolution of 3.6 nm.

In Fig. S2 there is a series of SEM images, where one can clearly see the orthorhombic  $\text{K}_2\text{YbF}_5$  single crystal, whose face points to the two-dimensional layer growth of the crystals under hydrothermal conditions causing their optical quality.



**Fig. S2.** SEM images of  $\text{K}_2\text{YbF}_5$  crystal at 23x (left), 70x (middle) and 2000x (right)

Finally we have carried out a high precision microanalysis to detect the elements of the crystalline matrix, Fig S3. Obtained results have showed that the atomic proportion of K, Yb and F is 26.75:14.5:58.6 (see inset), confirming the stoichiometric ratio of the synthesized  $K_2YbF_5$  crystals.

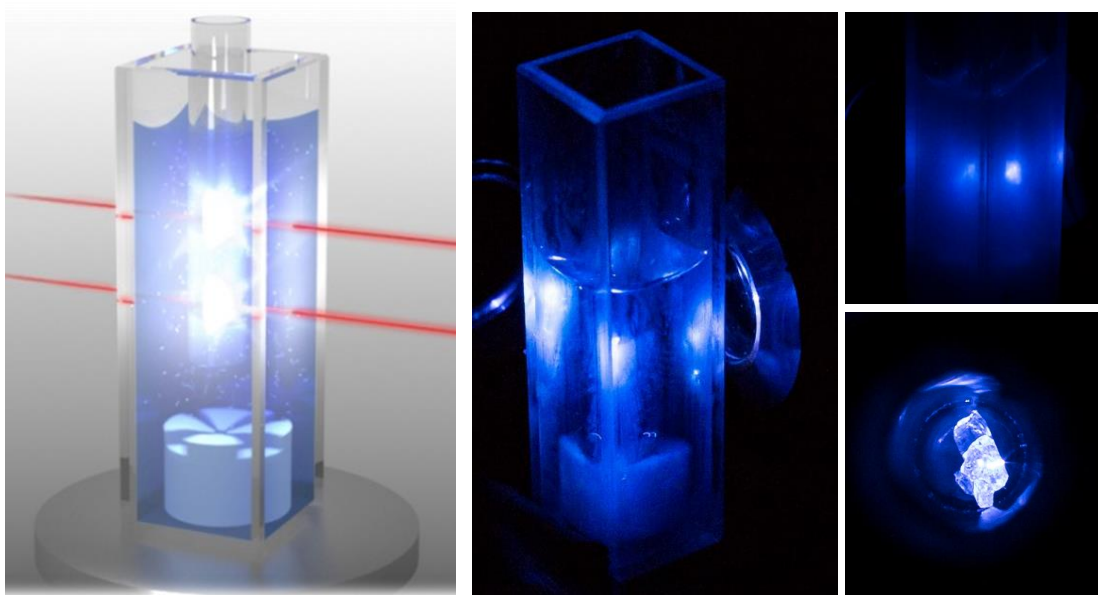


**Fig. S3.** EDX microanalysis of the  $K_2YbF_5$  crystal.

#### *About up-conversion driven photocatalytic experiments*

The initial methylene solution was prepared in quartz cuvettes. Then a piece of the UC  $K_2YbF_5:Tm^{3+}$  crystal (of about  $1.0\text{ mm}^3$  size) was inserted inside a quartz tube (transparent up to the UV range, to avoid diminishment of the crucial 290 to 360 nm UC emissions), which was placed in the middle of the cuvette filled with the MB- $TiO_2$  aqueous solution. Then two 980 nm laser diode beams, with an output power up to 300 mW, were focused on the UC  $K_2YbF_5:0.2\text{ at\% }Tm^{3+}$  crystal, yielding to intense UV-Blue UC emissions that passed through the solution during the experiments, as it can be seen in the 3D-computer designed sketch and photographs presented in Fig S4.

At this point it is very important to remark that control experiments were also carried with the MB- $TiO_2$  solution under radiation from the same 980 nm laser but without any UC crystal inside the quartz cuvette, and no photocatalytic MB degradation was observed at all. These tests have allowed us to determine that there are not any unexpected activation of the  $TiO_2$  photocatalyst by NIR light as well as other undesirable thermal effects caused by laser heating of aqueous solution.



**Fig. S4.** Experimental setup for up-conversion driven photocatalytic experiments by using two 980 nm laser diode beams focused on the UC  $\text{K}_2\text{YbF}_5:0.2 \text{ at\% Tm}^{3+}$  crystal, yielding to intense UV-Blue UC emissions that passed through MB- $\text{TiO}_2$  aqueous solution.

*About upconversion efficiency (yield) of  $\text{K}_2\text{YbF}_5:\text{Tm}^{3+}$  crystals:*

We have applied a simple quantitative method for estimating of UC yield of these family of UC samples, proposed in a pioneer paper by Suyver et al. (J. Lumin., 2006, 117, 1), to determine the number of up-converted photons relative to the total number of NIR excitation photons absorbed by the presented  $\text{K}_2\text{YbF}_5:\text{Tm}^{3+}$  phosphor, see Ref 14. In particular we have obtained a value of around 36% for the UC crystal representing the fraction of the total UC photon emitted from the crystal which can activate the  $\text{TiO}_2$  and  $\text{SrTiO}_3$  photocatalysts by generating electron-hole pairs to overcome corresponding bandgaps. Nevertheless, absolute quantum efficiencies of these samples in comparison of extensively used well-known efficient  $\text{NaYF}_4$ -based samples, this family  $\text{K}_2\text{YbF}_5$  phosphors, in particular doped with  $\text{Tm}^{3+}$ , give rise to larger amount of UV-blue up-converted photons in the range of interest for our photocatalytic applications, that is, from 290 to 360 nm, exactly necessary to bridge the gap of the photocatalysts used in our work. These larger intensities of UV-blue UC emissions, in comparison with typically observed ones in  $\text{NaYF}_4:\text{Yb}^{3+}$  phosphors doped with  $\text{Tm}^{3+}$ , represents one of the main advantage of our UC composition aimed at photocatalytic enhancement.