## Supplementary



Figure S1: Schematic energy level diagram of (VO<sub>4</sub>)<sup>3-</sup> and Yb<sup>3+</sup> in YbVO<sub>4</sub>.<sup>8,20</sup> Black arrows show excitation, while the green and red arrows
5 show emission processes. Relaxation from the <sup>1</sup>T<sub>1,2</sub> excited states to the <sup>3</sup>T<sub>1,2</sub> excited states is most likely non-radiative (short dash). From the <sup>3</sup>T<sub>1,2</sub> excited states, energy can transfer to two nearby Yb<sup>3+</sup> via CET (dashed arrows). The positions of the energy levels are approximate.

 $\ensuremath{\mathsf{OceanOptics}}$  USB4000 photo spectrometer. No corrections have been made.



Figure S3: FE-SEM image of a sample with a 1:3 pulse ratio of Yb(thd)<sub>3</sub> and VO(thd)<sub>2</sub>. The amorphous material is expected to consist mostly of excess  $V_2O_5$ .



10 Figure S2: Normalized PL spectra of samples with a 1:3 pulse ratio of  $Yb(thd)_3$  and  $VO(thd)_2$  annealed at 600-700 °C. Measured with an 20



Figure S4: Elemental mapping of a non-crystalline area on a sample with 30 pulse% Yb(thd)<sub>3</sub>, showing that the amorphous material consists of vanadium, oxygen and carbon and contains no ytterbium.



**Figure S5:** Absorption spectra of some of the as-deposited samples deposited on fused silica. The absorption of the fused silica substrate has not been subtracted.