5 Support Information

Thermal analysis of compound $Tb(H_3PTC)_3$. Thermal analysis was carried out in a Shimadzu TGA-60 equipment ($10°C\ min^{-1}$, under air flow, 50 mL min^{-1}). TG curve (Figure S. 1) showed a significant weight loss starting at $400°C$, temperature up to $525°C$, related to the thermal decomposition of the ligand. After complete decomposition, a stable residue (12.9%) assigned to Tb_2O_3 was formed (calc. 13.1%).

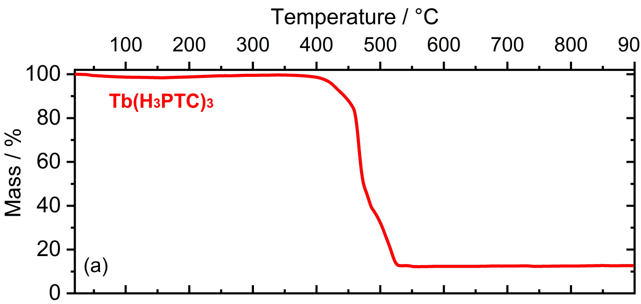

Figure S. 1 The TGA measurements show $Tb(H_3PTC)_3$'s thermal stability until $\sim 700K$.

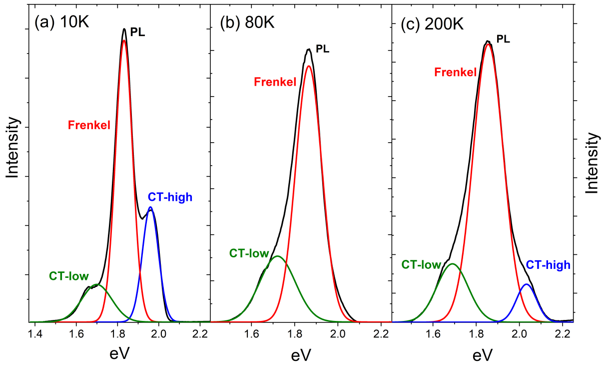

Figure S. 2 Photoluminescense measurements varying with temperature, at (a) 10 K, (b) 80 K and (c) 200 K, and gaussian-fit-peaks for each exciton process.

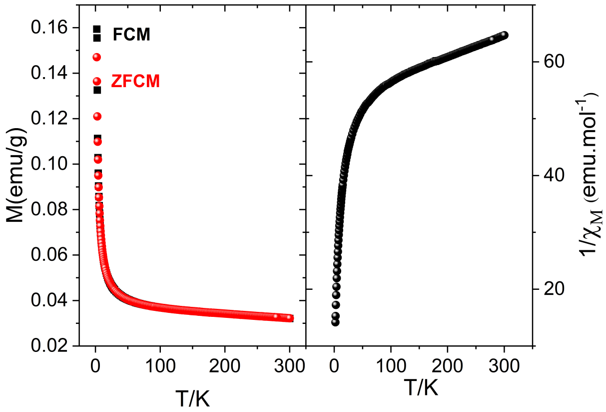

Figure S. 3 Magnetization measurements on $Tb(H_3PTC)_3$. Field-cooled magnetization (FCM) and Zero-field-cooled magnetization (ZFCM)(left) and the calculated inverse magnetic susceptibility as a function of temperature from the previous (right). A straight line for $1/\chi(T) \times T$ would indicate a paramagnetic material. Instead, the curve shows a magnetic ordering. The results indicate that there is no blocking temperature.

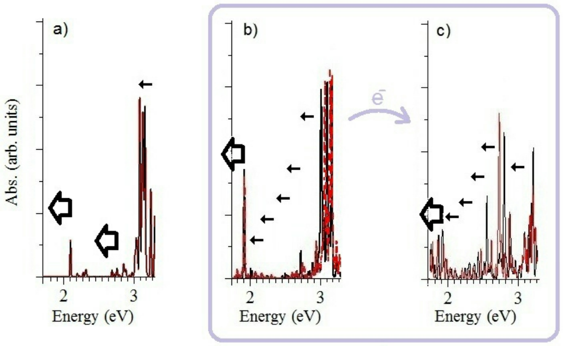

Figure S. 4 Absorption of $Tb(H_3PTC)_3$ calculated by DFT (different colors, red or black, for different spin states): a) neutral molecule, b) positively charged molecule, c) negatively charged molecule. Little black arrows represent exciton thermalization via phonons. Big hollow arrows represent bound exciton formation (the energy of the emitted photons lies at the tip). Whenever (b) happens, (c) can happen as a consequence, unless a phonon scatters the transferring electron, providing two new different pathways to thermalization, both yielding photons with lower energy than in neutral molecules.

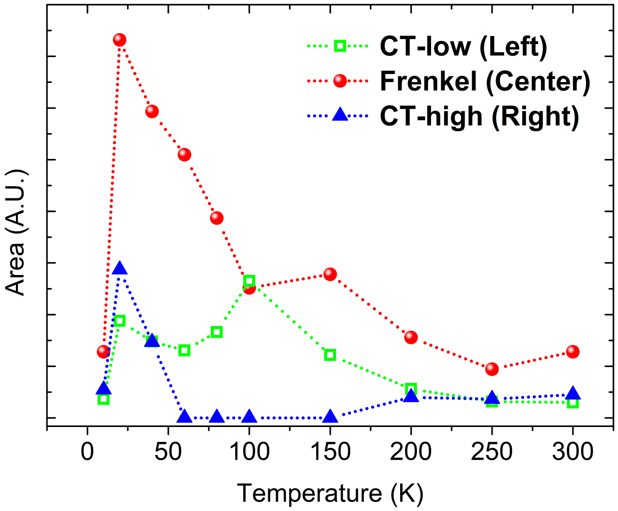

Figure S. 5 The integrated area of each PL process as a function of sample temperature