Supporting Information for "From arm-shaped layers to a new type of polythreaded array: a two fold interpenetrated three-dimensional network with the rutile topology, Chao Qin, Xinlong Wang, Lucia Carlucci, Mingliang Tong, Enbo Wang,* Changwen Hu and Lin Xu, *Chemical Communications*"

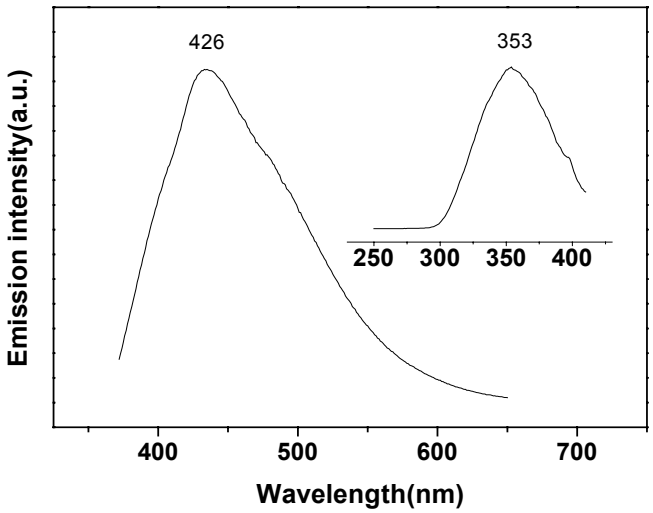
SI1: The synthesis of compound 1:

Because pH values of the reaction solution under hydrothermal reaction have a profound influence on the reaction outcome, we did parallel experiment during the course of synthesis, i.e. the dose of reaction material is invariable, while adjusting pH value of the reaction solution through changing the content of triethylamine. First, we did exploratory experiment in the wide range of pH (i.e. 2.5, 3.5, 4.5, 5.5, 6.5, 7.5), the results of these experiment are as following: the phenomena of all the reactor are white powder or crystallite except that of pH = 6.5, in which there are light-yellow crystals in low yield. But after testing, we found that it is the same as that of a reported structure (App. Organometal. Chem. 2003, 17, 739). Comparing and analyzing the reaction condition, we drew a conclusion, that is, the pH values of reaction solution shouldn't be in the range of neutrality or near alkalinity, because BTC is easily deprotonized to form 3D structure under such conditions, not 2D layer. For this reason, we did the second experiment (pH=2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, respectively), the results showed that: when pH≤4.0, only plenty of powder can be obtained, while when 4.5≤pH≤5.5, there are crystallite appeared. Based on the above results, we did experiment in the range of 4.5≤pH≤5.5, fortunately after adjusting pH

values by try and error, we finally get the aimed compound ($pH_{\text{before reaction}} = 4.7$, $pH_{\text{after reaction}} = 5.8$).

$[Zn(HBTC)(4,4'\text{-bpy})]_n$ (1). Compound **1** was synthesized from the reaction mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.5mmol), H_3BTC (0.6mmol), 4,4'-bpy (0.5mmol), triethylamine (1mmol) and water (10ml) in a 23ml Parr Teflon-lined stainless steel vessel, under autogenous pressure at 160℃ for 5 days and then cooled to room temperature at a rate of 10℃/h. Light-yellow crystals of compound **1** were obtained. The initial pH value of the reaction solution was ca. 4.7, and the final pH value was ca. 5.8. Elemental analysis found: C, 52.83%; H, 2.47%; N, 5.26%; Zn, 14.93%. Calcd. for: C, 53.06%; H, 2.79%; N, 5.59%; Zn, 15.22%.

SI2: Solid state emission spectra of compound 1 at room temperature.



SI3: Criterion adopted for the simplification