

Supporting Information

The Tb(III) postsynthetic functional coordination polymer coatings on ZnO micronano arrays and application in small molecule sensing

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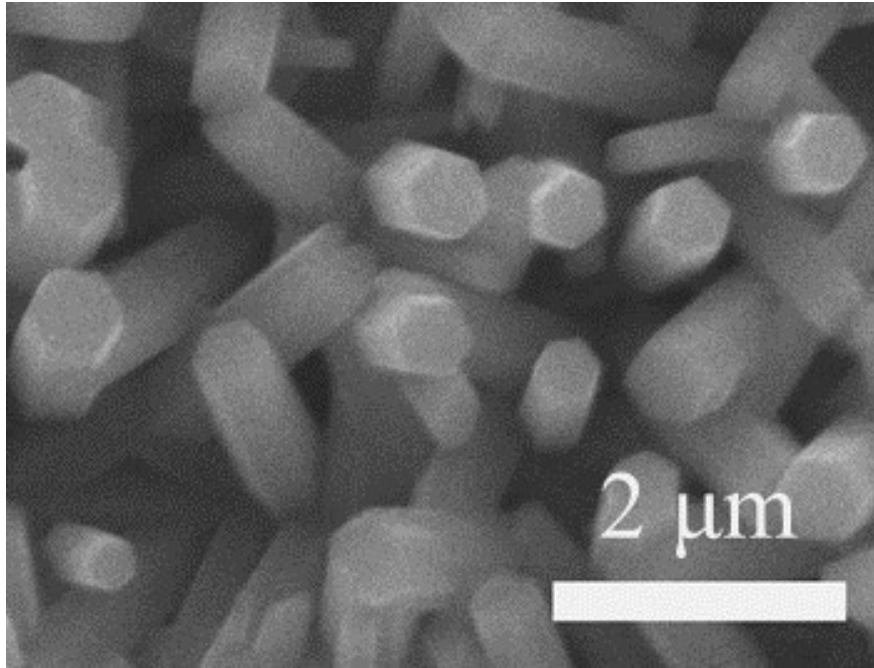


Figure S1. Top view of SEM image of ZnO micronano arrays.

1. Preparation of the Hybrid Micronano CP/ZnO Coatings

Synthesis procedure of the hybrid micronano **Zn(BTC)/ZnO** coating is as follows. 9 mM 1,3,5-benzenetricarboxylate, 12.5 mM $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.2 mL triethylamine in 10 mL ethanol was mixed followed by magnetic stirring for 10 minutes, the solid particles were filtered. The ZnO coated substrate was immersed facing down in the above filtrate. Zn(BTC) growth on the ZnO coated substrate proceeded for 5 h at 100 °C in a sealed Teflon lined autoclave. The CP-coated slide was removed from the solution and rinsed with ethanol to remove loose precipitate from the slide.

Synthesis procedure of the hybrid micronano **Zn(NDC)/ZnO** coating is as follows. 14 mM 2,6-naphthalenedicarboxylate, 46 mM $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.5 mL NaOH (0.5M) in 10 mL deionized water was mixed followed by magnetic stirring for 10 minutes, the solid particles were filtered. The ZnO coated substrate was immersed facing down in the above filtrate. Zn(NDC) growth on the ZnO coated substrate proceeded for 5 h at 80 °C in a sealed Teflon lined autoclave. The CP-coated slide was removed from the solution and rinsed with deionized water to remove loose precipitate from the slide.

2. Preparation of the Hybrid Luminescent Tb(III)@CP/ZnO Coatings

The lanthanide doped hybrid micronano CP/ZnO coatings: The **Zn(BTC)/ZnO** was immersed in the ethanol solutions of terbium nitrate (20 mL, 0.01M). After immersing for 3 days, the coating was washed with ethanol several times to remove residual Tb^{3+} ion on the surface, to form Tb^{3+} doped hybrid luminescent coating of **Tb(III)@Zn(BTC)/ZnO**. Synthetic procedure of the **Tb(III)@Zn(NDC)/ZnO** was the same as above described except the **Zn(BTC)/ZnO** was replaced by the **Zn(NDC)/ZnO**.

3.

The detection limit was calculated based on the luminescence titration experiment. To determine the S/N ratio, the emission intensity of **Tb@MOF-5/ZnO** without acetone was measured for 11 times and the standard deviation of blank measurements was determined. The detection limit is then calculated with the following equation.

$$\text{LOD} = 3\delta / K_{\text{SV}}$$

Where δ is the standard deviation of blank measurements, K_{SV} is the slope of Stern-Volmer curve.

$$K_{SV}=6.7, \delta=\sqrt{\frac{\sum (F_0 - F_1)^2}{N-1}}=0.2 (N=11),$$

LOD = $3\delta/K_{SV} \approx 0.08$ M (F_0 is the luminescence intensity of **Tb(III)@MOF-5/ZnO**; F_1 is the average of the F_0).

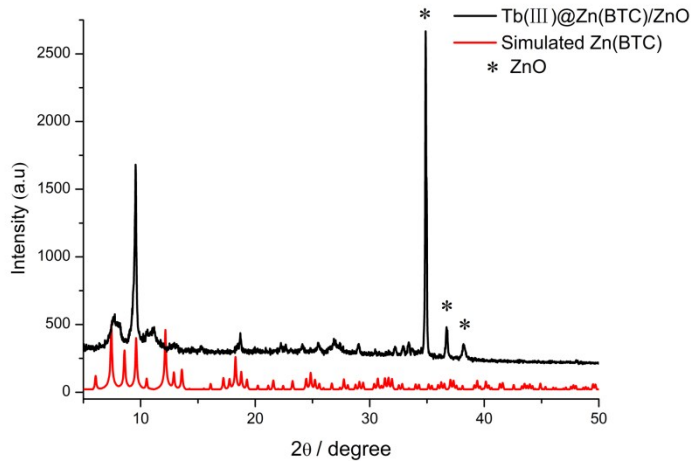


Figure S2. PXRD of the simulated Zn(BTC) and the **Tb(III)@Zn(BTC)/ZnO**.

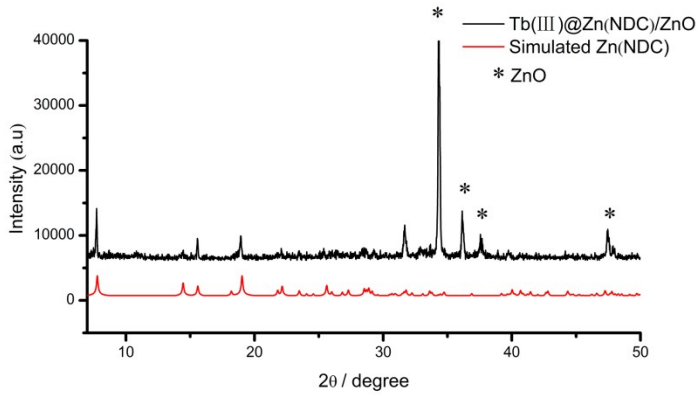


Figure S3. PXRD of the simulated Zn(NDC) and the **Tb(III)@Zn(NDC)/ZnO**.

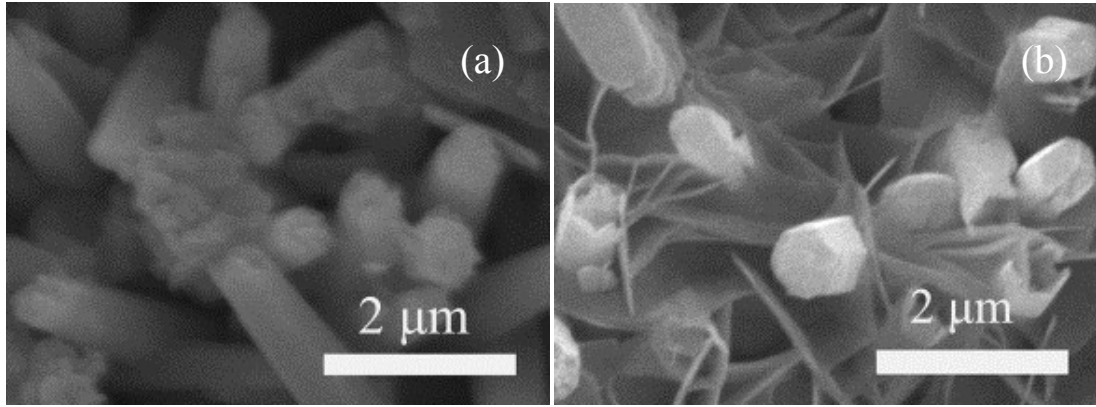


Figure S4. (a) SEM of Zn(BTC)/ZnO , (b) $\text{Tb(III)@Zn(BTC)/ZnO}$.

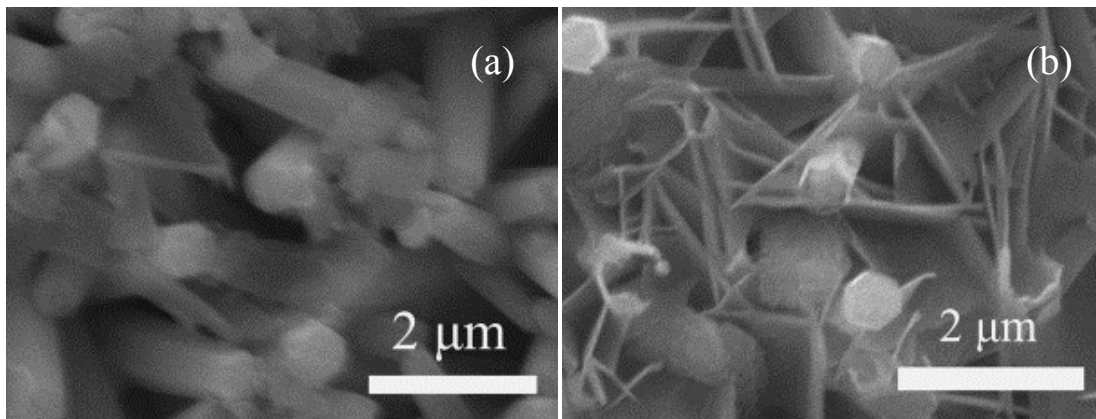


Figure S5 (a) SEM of Zn(NDC)/ZnO , (b) $\text{Tb(III)@Zn(NDC)/ZnO}$.

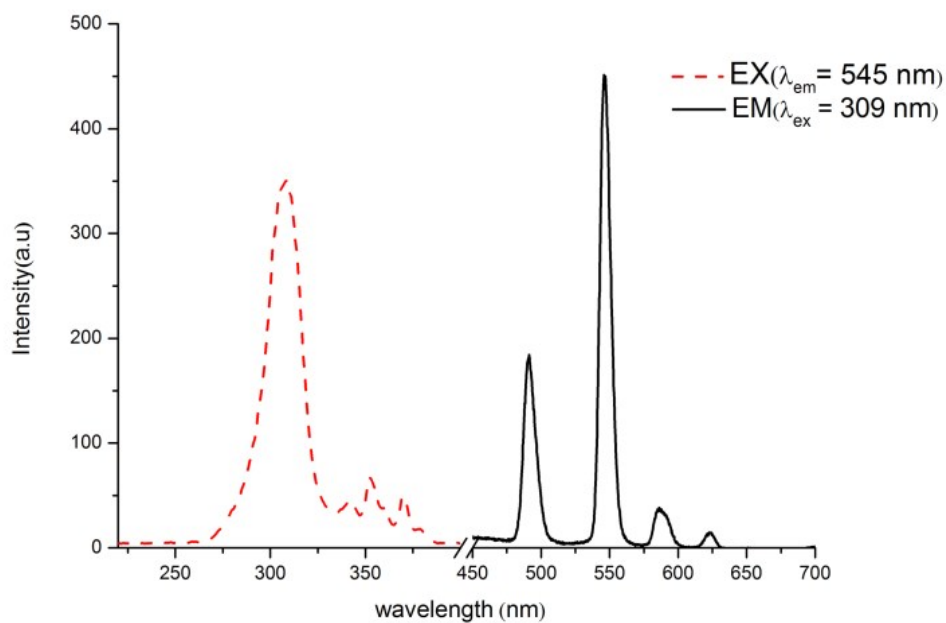


Figure S6. The excitation (dashed) and emission spectra (solid) of the **Tb(III)@Zn(BTC)/ZnO**.

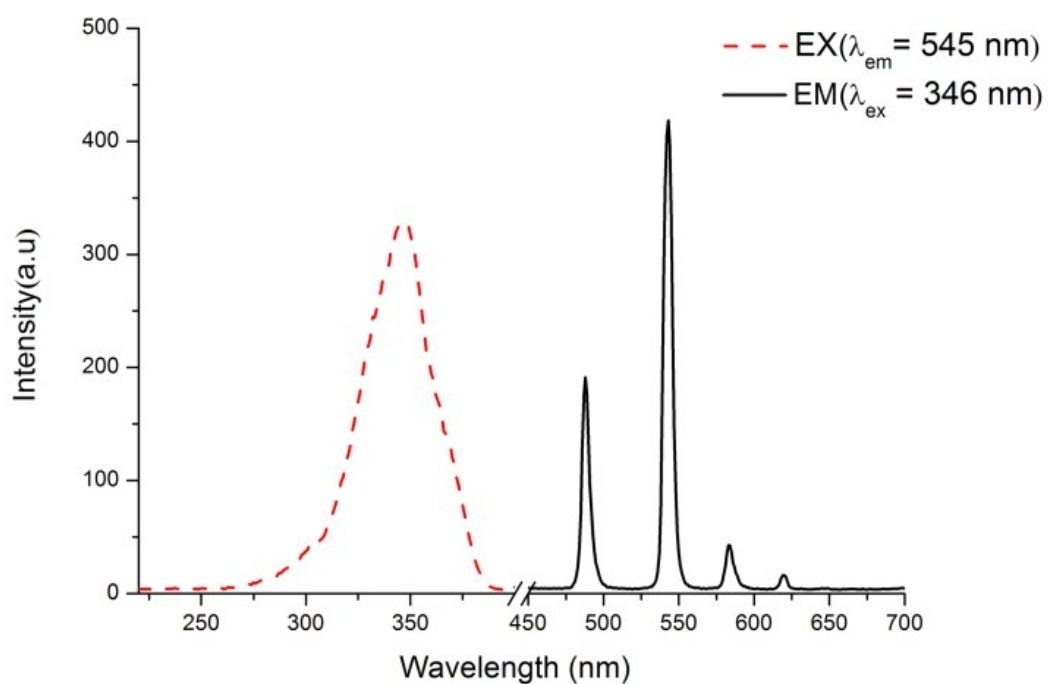


Figure S7. The excitation (dashed) and emission spectra (solid) of the **Tb(III)@Zn(NDC)/ZnO**.

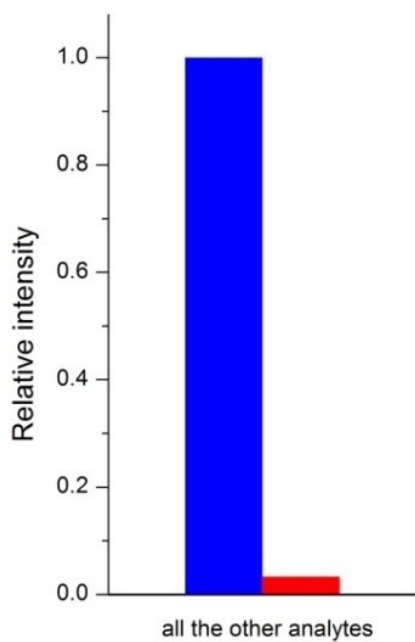


Figure S8. The $^5D_4 \rightarrow ^7F_5$ transition intensities of the **Tb(III)@MOF-5/ZnO** on the addition of all the other analytes (6 vol% each, blue) and subsequent addition of acetone (6 vol%, red)($\lambda_{exc} = 299$ nm).

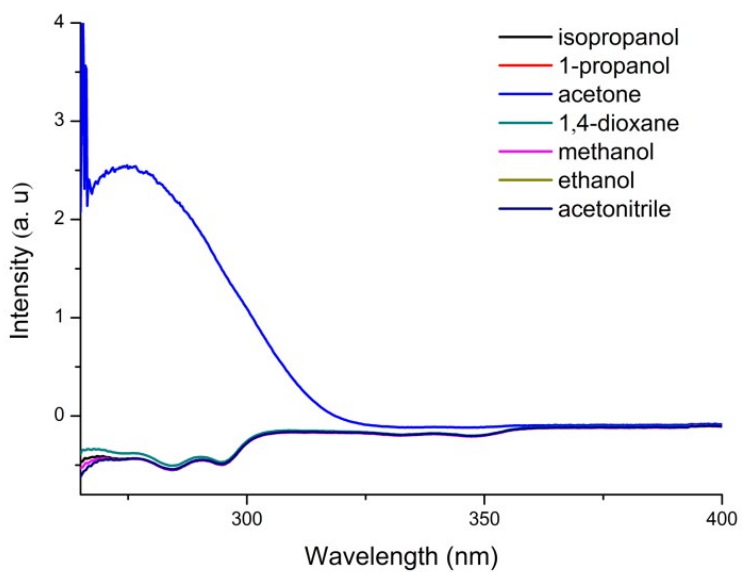


Figure S9. UV absorption spectra of different solvent molecules (1 vol%) in DMF.

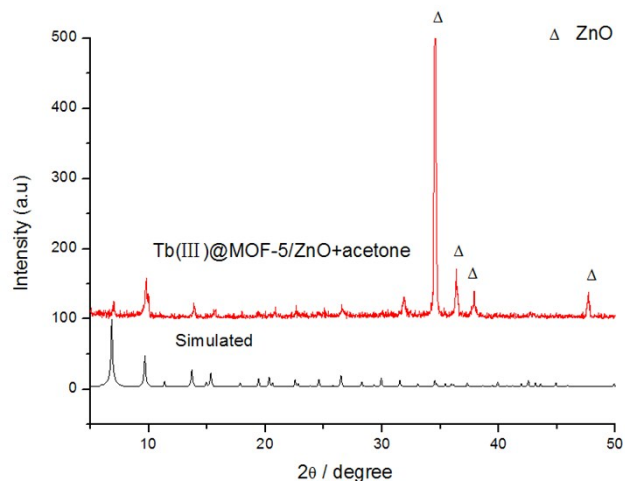


Figure S10 PXRD patterns of the simulated MOF-5, **Tb(III)@MOF-5/ZnO** treated with acetone.

Table S1 Ratio of metal ions (Zn:Tb) in **Tb(III)@Zn(BTC)/ZnO** and **Tb(III)@Zn(NDC)/ZnO**.

Sample	(Zn:Tb)
Tb(III)@Zn(BTC)/ZnO	65:1
Tb(III)@Zn(NDC)/ZnO	30:1