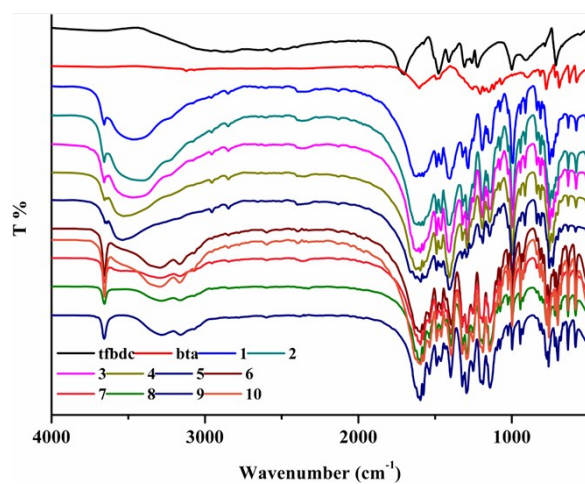


## Electronic Supplementary Information

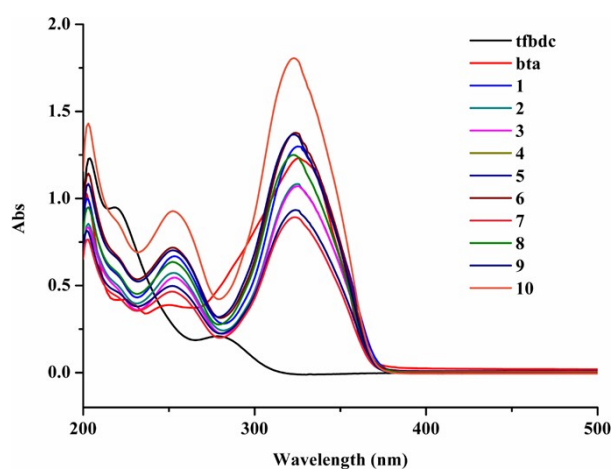
### **Structure, color-tunable luminescence, and UV-vis/NIR benzaldehyde detection of lanthanide coordination polymers based on two fluorinated ligands**

Xu Yao,<sup>‡</sup> Xinyu Wang,<sup>‡</sup> Yongqiang Han, Pengfei Yan, Yuxin Li and Guangming Li\*

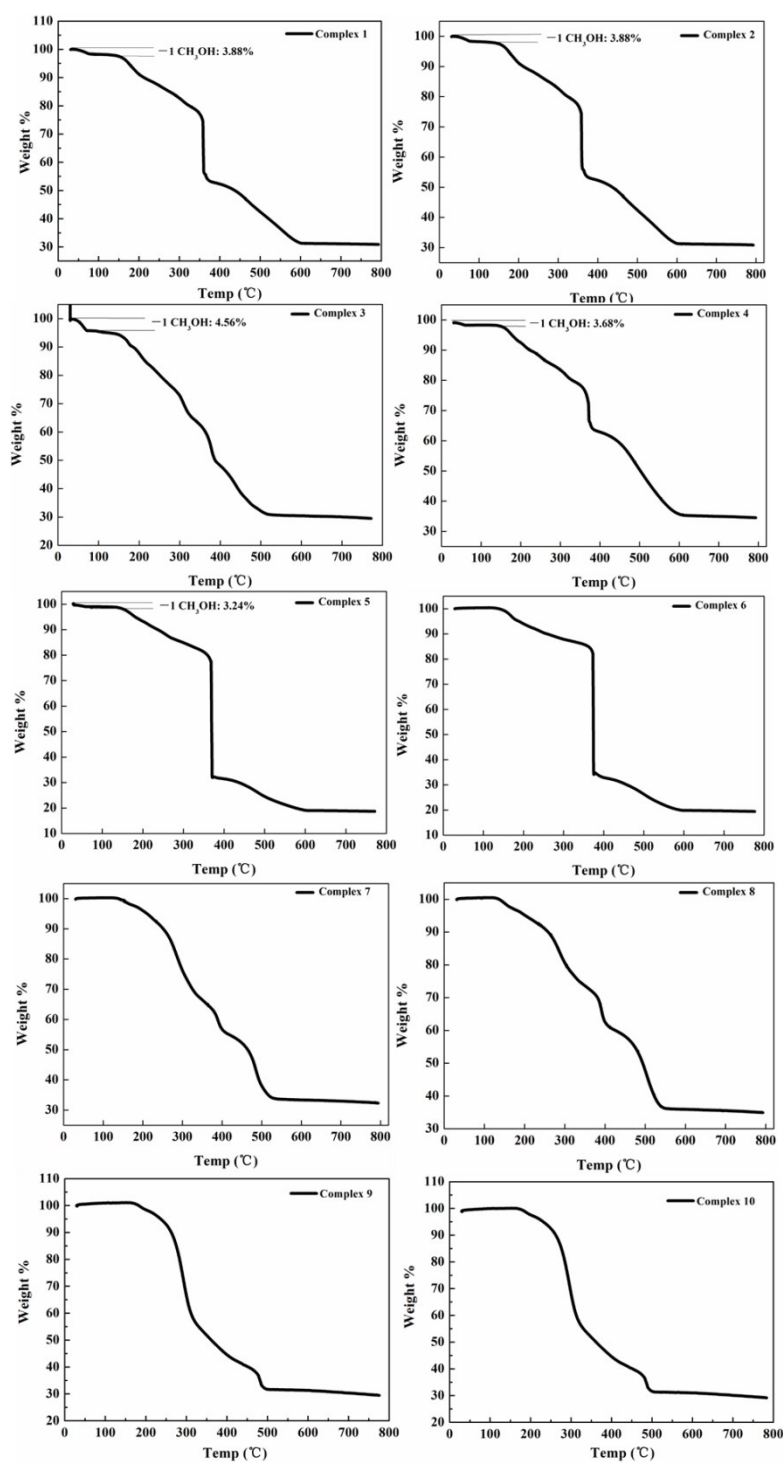
*Key Laboratory of Functional Inorganic Material Chemistry (MOE), School of Chemistry and Materials Science, Heilongjiang University, No. 74, Xuefu Road, Nangang District, Harbin 150080, P. R. China. E-mail: gmli@hlju.edu.cn*



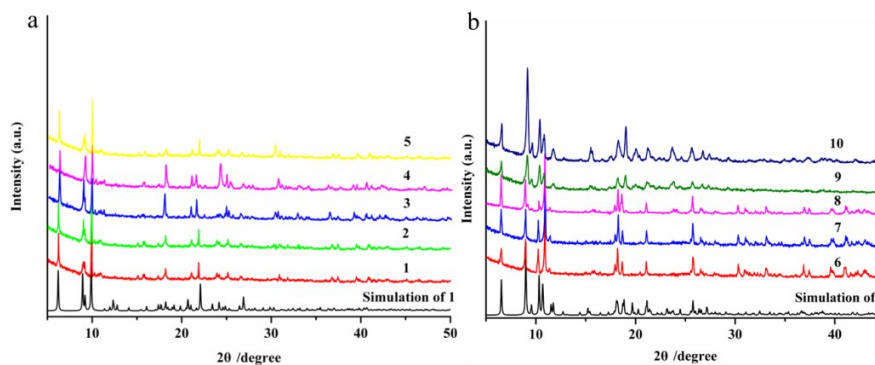
**Fig. S1** Infrared spectra of two ligands and complexes 1–10.



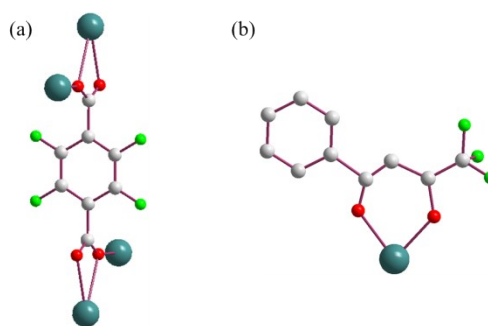
**Fig. S2** Ultraviolet spectra of two ligands and complexes 1–10.



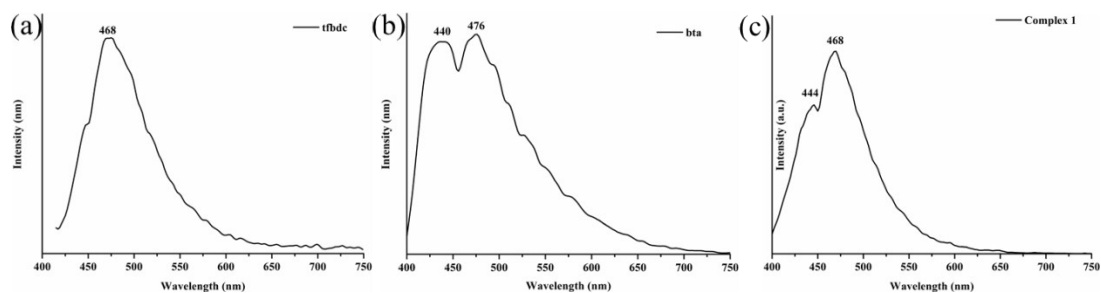
**Fig. S3** TG curves of complexes 1–10.



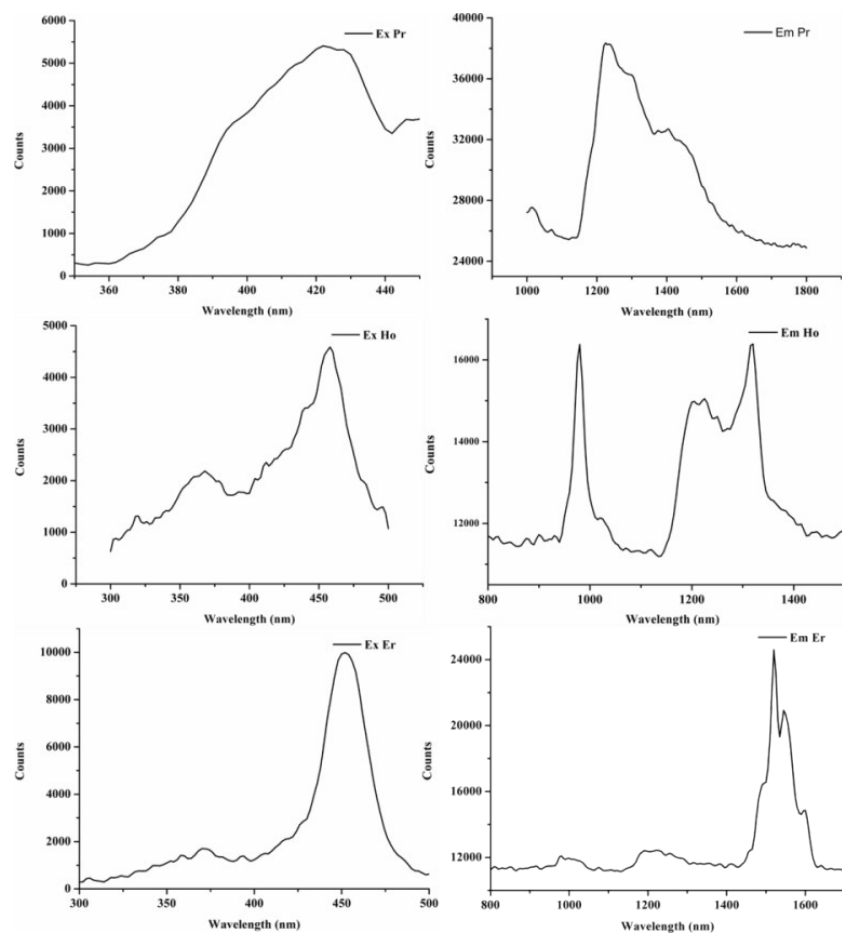
**Fig. S4** (a) PXRD patterns of complex **1** simulated from the X-ray single-crystal structure and as-synthesized samples of complexes **1–5**. (b) PXRD patterns of complex **6** simulated from the X-ray single-crystal structure and as-synthesized samples of complexes **6–10**.



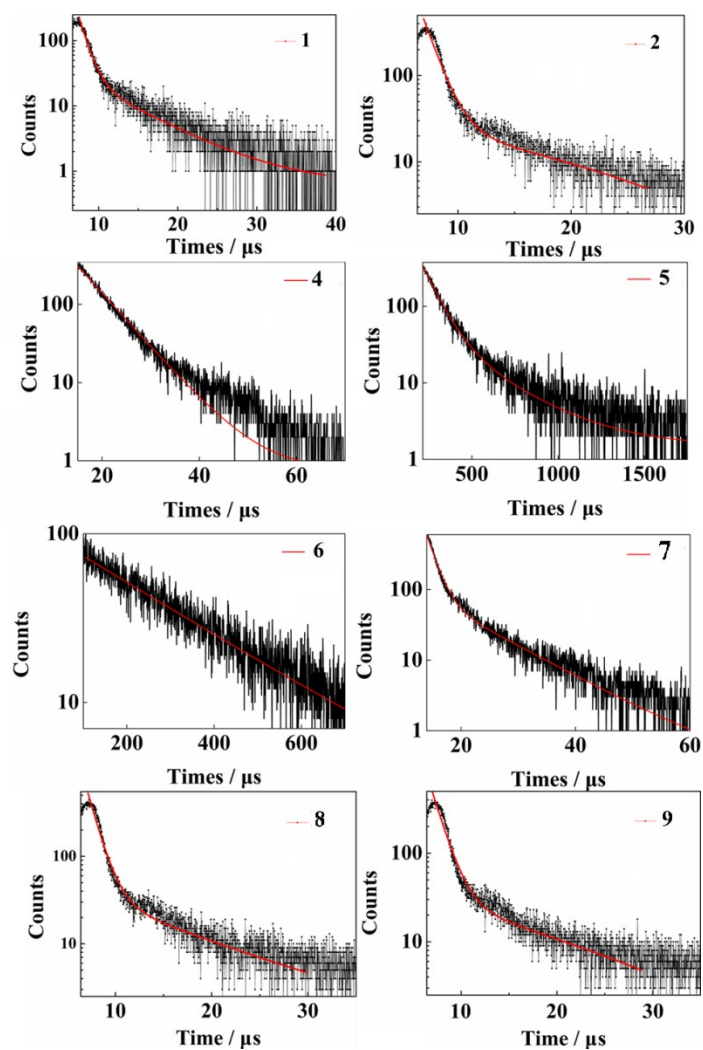
**Fig. S5** The coordinating modes of tfbdc (a) and bta (b) in complexes **1–10**.



**Fig. S6** Solid state emission spectra of two ligands and complex **1**.



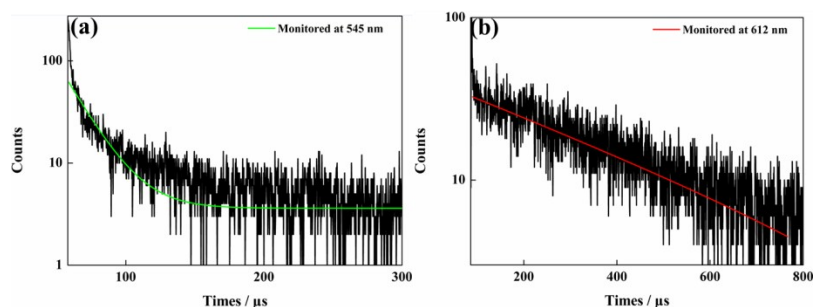
**Fig. S7** Solid state excitation (left) and emission (right) spectra of complexes **2**, **8** and **9**.



**Fig. S8** Room-temperature luminescence decay curves of complexes **1**, **2** and **4–9**.

**Table S1** Elemental analysis of lanthanide ions by ICP for complex **11**

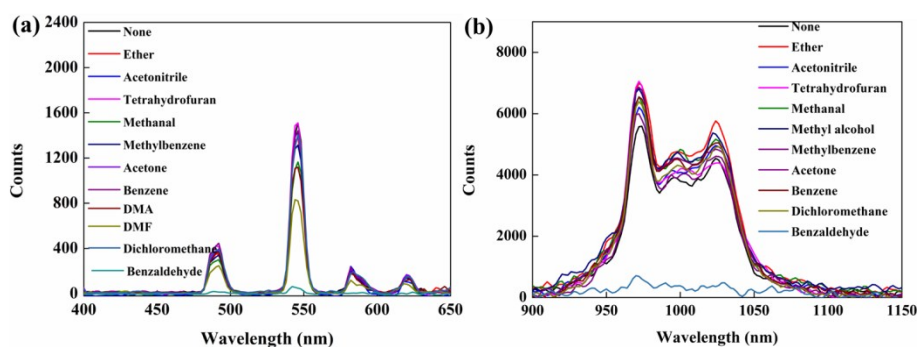
| Comp.        | Complex <b>11</b> |     |      |
|--------------|-------------------|-----|------|
|              | La                | Eu  | Tb   |
| Wt % (Found) | 88.0              | 2.0 | 10.0 |
| Mol %        | 86.3              | 2.6 | 11.1 |



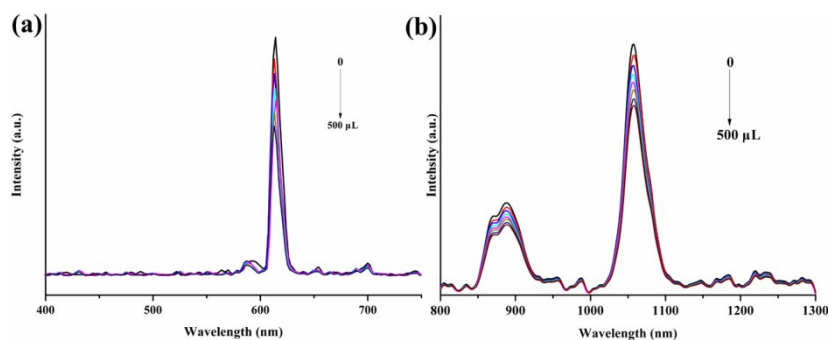
**Fig. S9** Room-temperature luminescence decay curves of complex **11** (monitored at 545 and 612 nm).

**Table S2** Luminescence lifetime and quantum yield of complexes **1–10** and their analogs.

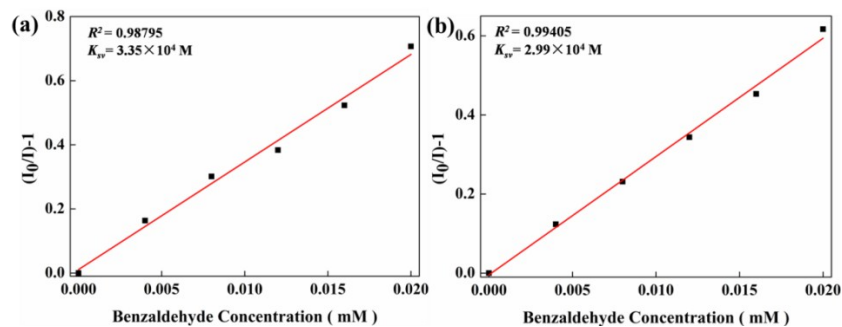
| Complexes | $\tau$ ( $\mu$ s) | $\Phi$ (%) | Complexes <sup>1</sup>                                   | $\tau$ ( $\mu$ s) | $\Phi$ (%) | Complexes <sup>2</sup>                        | $\tau$ ( $\mu$ s) | $\Phi$ (%) |
|-----------|-------------------|------------|----------------------------------------------------------|-------------------|------------|-----------------------------------------------|-------------------|------------|
| <b>1</b>  | 0.53;3.14         | 1.90       | -                                                        | -                 | -          | -                                             | -                 | -          |
| <b>2</b>  | 0.57;8.34         | 6.80       | Pr(tfbdc) <sub>1.5</sub> (H <sub>2</sub> O)              | 10.43             | 20.57      | -                                             | -                 | -          |
|           |                   |            | Pr(tfbdc) <sub>1.5</sub> (H <sub>2</sub> O) <sub>2</sub> | 2.53              | 5.00       | -                                             | -                 | -          |
| <b>3</b>  | 11.35             | 4.20       | Nd(tfbdc) <sub>1.5</sub> (H <sub>2</sub> O)              | 2.20              | 0.81       | -                                             | -                 | -          |
|           |                   |            | Nd(tfbdc) <sub>1.5</sub> (H <sub>2</sub> O) <sub>2</sub> | 1.50              | 0.56       | -                                             | -                 | -          |
| <b>4</b>  | 6.31              | 3.29       | Sm(tfbdc) <sub>1.5</sub> (H <sub>2</sub> O)              | 1.61;5.52         | 0.73       | -                                             | -                 | -          |
|           |                   |            | <sup>2</sup>                                             |                   |            | -                                             | -                 | -          |
| <b>5</b>  | 159.80            | 10.17      | Eu(tfbdc) <sub>1.5</sub> (H <sub>2</sub> O) <sub>2</sub> | 186.93            | 10.39      | Eu(tfbdc)(NO <sub>3</sub> )(DMF) <sub>2</sub> | -                 | 53.00      |
|           |                   |            |                                                          |                   |            | Eu(tfbdc)(CH <sub>3</sub> COO)(FA)            | -                 | 10.00      |
|           |                   |            |                                                          |                   |            | <sup>3</sup>                                  |                   |            |
| <b>6</b>  | 274.10            | 15.74      | Tb(tfbdc) <sub>1.5</sub> (H <sub>2</sub> O) <sub>2</sub> | 916.87            | 30.56      | -                                             | -                 | -          |
| <b>7</b>  | 5.20              | 2.10       | Dy(tfbdc) <sub>1.5</sub> (H <sub>2</sub> O) <sub>2</sub> | 1.72;6.73         | 0.89       | -                                             | -                 | -          |
| <b>8</b>  | 0.64;3.98         | 0.56       | Ho(tfbdc) <sub>1.5</sub> (H <sub>2</sub> O) <sub>2</sub> | 1.42              | 0.11       | -                                             | -                 | -          |
| <b>9</b>  | 0.66;5.90         | 1.44       | Er(tfbdc) <sub>1.5</sub> (H <sub>2</sub> O) <sub>2</sub> | 1.67;7.56         | 1.79       | -                                             | -                 | -          |
| <b>10</b> | 7.94              | 0.40       | Yb(tfbdc) <sub>1.5</sub> (H <sub>2</sub> O) <sub>2</sub> | 1.48;7.21         | 0.26       | -                                             | -                 | -          |



**Figure S10** Luminescence of complex **6** (a) and **10** (b) dependence on the various analytes (300  $\mu$ L) dispersed in ethanol upon excitation at 362 and 360 nm, respectively.



**Fig. S11** (a) Luminescence spectra of **5**@EtOH in the presence of various amounts of benzaldehyde from 0 to 500  $\mu\text{L}$ . (b) Luminescence spectra of **3**@EtOH in the presence of various amounts of benzaldehyde from 0 to 500  $\mu\text{L}$ .



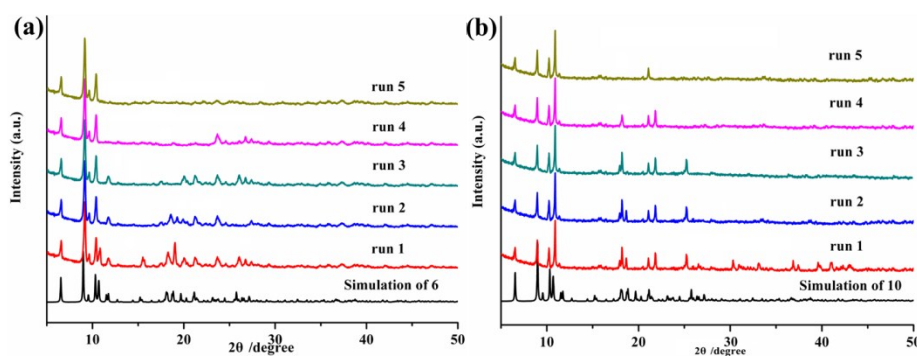
**Fig. S12** The Stern-Volmer plots for complexes **6** and **10** with benzaldehyde in the low concentration region. The solid lines represent fits to the concentration-resolved data using the Stern-Volmer equation.

**Table S3** Standard Deviation ( $\sigma$ ) calculation for complex **6** sensing benzaldehyde.

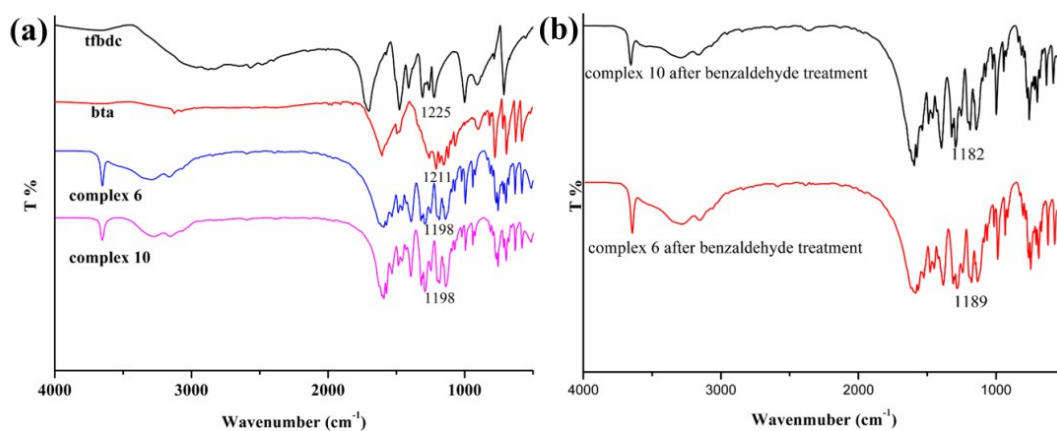
| Test                            | Fluorescence intensity (nm) |
|---------------------------------|-----------------------------|
| Test 1                          | 1500                        |
| Test 2                          | 1492                        |
| Test 3                          | 1512                        |
| Test 4                          | 1510                        |
| Test 5                          | 1492                        |
| Standard Deviation ( $\sigma$ ) | 8.61                        |

**Table S4** Standard Deviation ( $\sigma$ ) calculation for complex **10** sensing benzaldehyde.

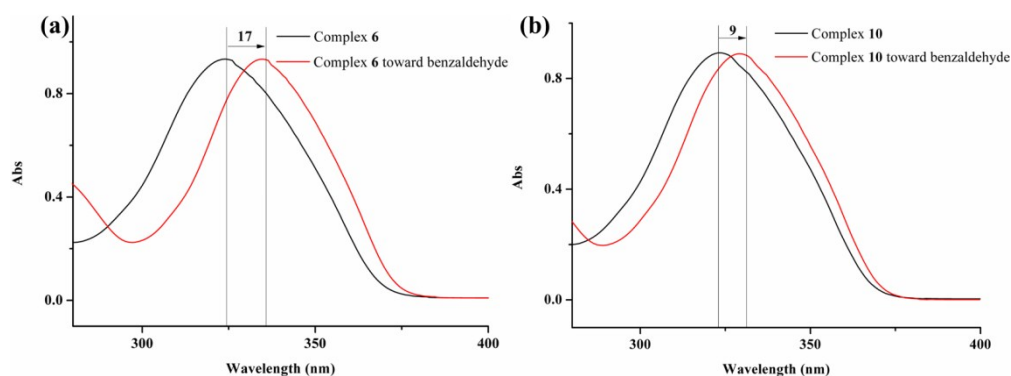
| Test                            | Fluorescence intensity (nm) |
|---------------------------------|-----------------------------|
| Test 1                          | 6916                        |
| Test 2                          | 6905                        |
| Test 3                          | 6931                        |
| Test 4                          | 6922                        |
| Test 5                          | 6913                        |
| Standard Deviation ( $\sigma$ ) | 8.73                        |

**Fig. S13** PXRD patterns of complexes **6** and **10** after detection of benzaldehyde for five cycles.**Table S5** Selected  $K_{sv}$  and detection limit for benzaldehyde for complexes **6**, **10** and other materials.

| Material                                            | $K_{sv}$ ( $M^{-1}$ ) | Detection limit (mM)  | Ref.      |
|-----------------------------------------------------|-----------------------|-----------------------|-----------|
| $[Sm_2Zn(abtc)_2(H_2O)_4] \cdot 2H_2O$ <sup>3</sup> | $1.36 \times 10^4$    | -                     | 3         |
| $[Nd_2(L)_2(DMAC)_2] \cdot nH_2O$ <sup>4</sup>      | $4.90 \times 10^4$    | $3.40 \times 10^{-4}$ | 4         |
| $[Tb(TFBDC)_{1.5}(H_2O)_2] \cdot H_2O$ <sup>1</sup> | $3.11 \times 10^4$    | $9.01 \times 10^{-4}$ | 1         |
| $[Eu(L)(HCOO)(H_2O)]_n$ <sup>5</sup>                | $1.29 \times 10^3$    | $1.10 \times 10^{-3}$ | 5         |
| $[Tb(L)(HCOO)(H_2O)]_n$ <sup>5</sup>                | $9.88 \times 10^2$    | $1.30 \times 10^{-3}$ | 5         |
| $\{[Tb(L)(H_2O)(DMF)] \cdot DMF\}_n$ <sup>6</sup>   | $5.22 \times 10^2$    | $0.54 \times 10^{-3}$ | 6         |
| Complex <b>6</b>                                    | $3.35 \times 10^4$    | $8.61 \times 10^{-4}$ | This work |
| Complex <b>10</b>                                   | $2.99 \times 10^4$    | $8.64 \times 10^{-4}$ | This work |



**Fig. S14** FT-IR spectra of complexes **6** and **10** before and after treatment with benzaldehyde.



**Fig. S15** UV-vis absorption spectra of complexes **6** and **10** before and after treatment with benzaldehyde.

## Reference

1. Y. Han, P. Yan, J. Sun, G. An, X. Yao, Y. Li and G. Li, *Dalton transactions*, 2017, **46**, 4642-4653.
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5. Z. Sun, M. Yang, Y. Ma and L. Li, *Crystal Growth & Design*, 2017, **17**, 4326-4335.
6. B. Ding, Y. Cheng, J. Wu, X. M. Wu, H. M. Zhang, Y. Luo, X. F. Shi, X. X. Wu, J. Z. Huo, Y. Y. Liu and Y. Li, *Dyes and Pigments*, 2017, **146**, 455-466.

