Electronic Supplementary Material (ESI) for Dalton Transactions. This journal is © The Royal Society of Chemistry 2017

Supporting Information

Luminescence, white-light and luminescent sensor of

tetrafluoroterephthalic lanthanide metal-organic frameworks

Yongqiang Han, Pengfei Yan, Jingwen Sun, Guanghui An, Xu Yao, Yuxin Li and Guangming Li*

Key Laboratory of Functional Inorganic Material Chemistry (MOE), P. R. China; School of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, P. R. China



Figure S1. IR spectra of the H₂L and complexes 1–16.



Figure S2. UV absorption spectra of the H_2L and complexes 1–16 in methanol solution.



Figure S3. Powder X-ray diffraction patterns and the simulated patterns of complexes 1–16.





Figure S4. TG-DSC curves of complexes 1–16.



Figure S5. Solid-state excitation spectra for complexes 1–13 at room temperature.



FigureS6. Solid-state emission spectra and decay curves for complexes 6-13.



Figure S7. Decay curves for complex 15.



Figure S8. Decay curves for complex 16.

Triplet state of the ligand and energy transfer

According to the Dexter theory, the match of the energy level between the triplet state energy of the ligand and the resonance emission energy level of the lanthanide ion is the most significant part for determining the luminescence of lanthanide complexes. Herein, the singlet (${}^{1}\pi\pi^{*}$) energy level of H₂TFBDC (318 nm, ${}^{1}\pi\pi^{*}$ = 31446 cm⁻¹) is estimated by referring to its wavelength of absorbance edge in the UV spectrum (Figure S2). The triplet (${}^{3}\pi\pi^{*}$) energy level of H₂TFBDC (484 nm: ${}^{3}\pi\pi^{*}$ = 21834 cm⁻¹) is determined by the low-wavelength emission peak of the phosphorescence of complex **8** at 77 K (Figure S9). Therefore, the energy gap ΔE (${}^{1}\pi\pi^{*}-{}^{3}\pi\pi^{*}$) of the H₂TFBDC is 9612 cm⁻¹. According to Reinhoudt's empirical rule, the intersystem crossing (ISC) process will be effective when the ΔE (${}^{1}\pi\pi^{*}-{}^{3}\pi\pi^{*}$) is at least greater than 5000 cm⁻¹. Thus, the ISC process is effective in this ligand (Figure S10).



Figure S9. Phosphorescence spectrum for complex 8 methanol solution at 77K.



Figure S10. Energy diagram showing lanthanide excited states and their position with respect the triplet states of H_2L sensitizers.



Figure S11. Luminescence spectra of complex 9 dispersed in various solvents when excited

at 346 nm.



Figure S12. The Stern–Volmer plot at low benzaldehyde concentrations. The luminescence intensity at 544 nm was used for analysis.



Figure S13. PXRD patterns of 9 after four recyclings.



Figure S14. PXRD patterns of 9 after immersing in ethanol and benzaldehyde for three days.



Figure S15. Decay curves of before (left) and after (right) benzaldehyde treatment (EtOH,

10mM, $20\mu L$, λ_{ex} = 346 nm).



Figure S16. FT-IR spectra of 9 before and after benzaldehyde treatment.

 Table S1. Elemental analysis of lanthanide ions by ICP for complexes 15 and 16

Comp.	15		16		
	Dy	Eu	Gd	Eu	Tb
Wt % (Found)	27.9	72.1	87.0	10.5	2.5
Mol %	28.1	71.9	87.1	10.3	2.6

Table S2. Standard deviation calculation				
	Fluorescence intensity			
Test 1	1261.48			
Test 2	1250.20			
Test 3	1258.13			
Test 4	1265.59			
Test 5	1268.43			
Standard Deviation (σ)	7.08			