Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Full-color emission of a Eu^{3+}-based mesoporous hybrid material modulated by Zn^{2+} ions: emission color changes for Zn^{2+} sensing via ion exchange approach

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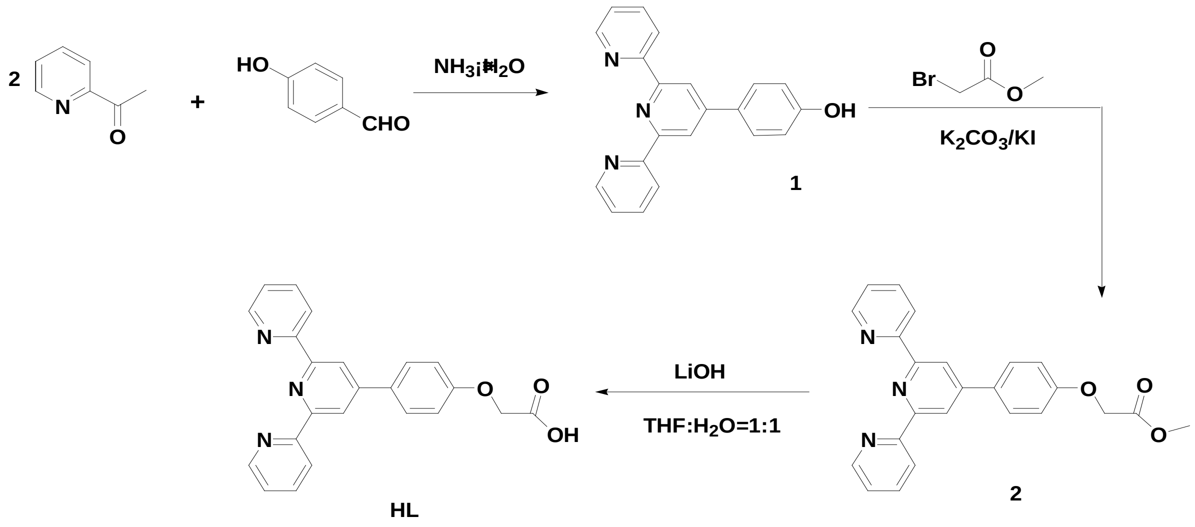
Synthesis of compound 1. Compound 1 was synthesized according to a previously reported method.[1] Briefly, 2-acetylpyridine (4.84 g, 40 mmol) was mixed and dissolved in ethanol solution (60 mL). 4-Hydroxyben-zaldehyde (2.44 g, 20 mmol) in ethanol solution (30 mL) was added, and the mixture was stirred for several minutes. Then, the mixture was added with an aqueous ammonium solution (50 mL, 25%) and stirred at 50 °C for 20 h. Then, a large amount of green solid was obtained when the pH of the solution was neutralized with hydrochloric acid (37%). The precipitate was collected and washed with ethanol to yield compound 1. The sample was dried overnight at 65 °C under vacuum.

Synthesis of compound 2. Compound 1 (1.3 g, 4 mol) and methyl bromoacetate (0.6 g, 4 mmol) were dissolved in anhydrous acetone (100 mL). Then, K_2CO_3 (1.1 g, 8 mmol) and KI (0.3 g, 1.8 mmol) were added to the solution, and the resulting mixture was refluxed for 8 h. Finally, the reaction mixture was concentrated and purified through flash column chromatography with $CHCl_2$/MeOH at 10/1 ratio as elution solvents. A white yellow solid was collected with a yield of 3.67 g (25%). ^1H NMR (500 M, $CDCl_3$, δ): 3.84 (s, 3H), 4.72 (s, 2H), 7.03–7.05(d, 2H, J=8.5 Hz), 7.34–7.36 (m, 2H), 7.87–7.89 (d, 2H, J=8.5 Hz), 8.66–8.72 (m, 6H).

Synthesis of 4´-(4-carboxy-methyleneoxyphenyl)-2,2´:6´,2″- terpyridinel (HL). Compound 2 (1.6 g, 4 mmol) and $LiOH·H_2O$ (5.03 g, 120 mmol) were dissolved in the mixture solvents of THF and H_2O (60 mL, v:v=1:1) and stirred for 72 h. The reaction mixture was concentrated and adjusted by HCl to pH=2–3. The resulting precipitate was collected and purified by chromatography on a silica gel with $CHCl_2/CH_3OH$ mixture (20/1, v/v) as elution solvents to obtain a white yellow powder. Yield: 0.34 g (21%). The synthesis processes of compounds 1, 2, and HL are presented in Scheme. S1 (ESI†). ^1H NMR (500 M, $CDCl_3$, δ): 4.63 (s, 2H), 7.08–7.09 (d, 2H, J=8Hz), 7.51–7.54 (m, 2H), 7.87–7.88 (d, 2H, J=8.5 Hz), 8.02–8.05 (m, 2H), 8.66–8.67 (m, 4H), 8.76–8.77 (d, 2H, J=4 Hz). Anal. Calcd for C23H17N3O3: C, 72.05; N, 10.96; H, 4.47; Found: C, 72.11; N, 10.92; H, 4.49.

Reference

1 S. X. Wang, W. H. Chu, Y. C. Wang, S. Y. Liu, J. C. Zhang, S. H. Li, H. Y. Wei, G. Q. Zhou and X. Y. Qin, *Appl. Organometal. Chem.*, 2013，**27**，373-379.



Scheme. S1 Synthesis processes of the compounds 1, 2 and organic liangd HL.

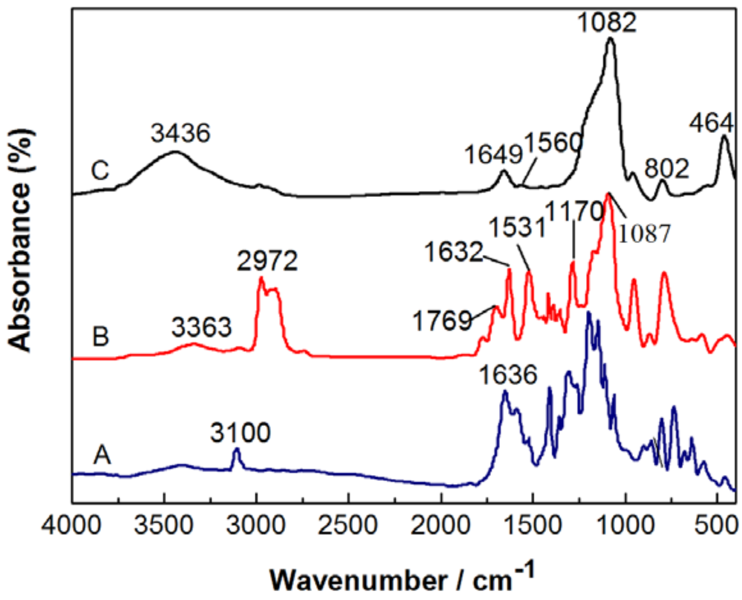


Fig. S1 FTIR spectra of TTA(A), TTA-Si (B) and TTA-Si modified mesoporous silica nanoparticle TTA-MSN (C).

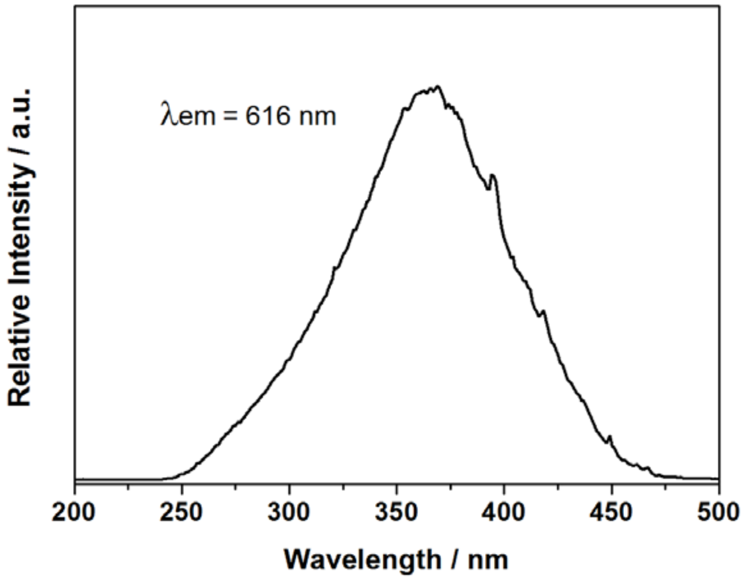


Fig. S2 The photoluminescent excitation spectrum of Eu(TTA-MSN)$_2$L.

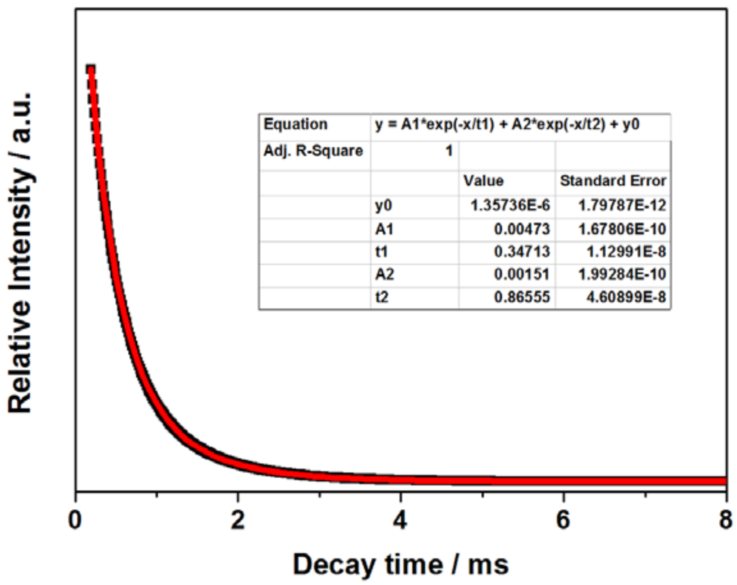


Fig. S3 Luminescence time decay curves for the sample Eu(TTA-MSN)$_2$L.

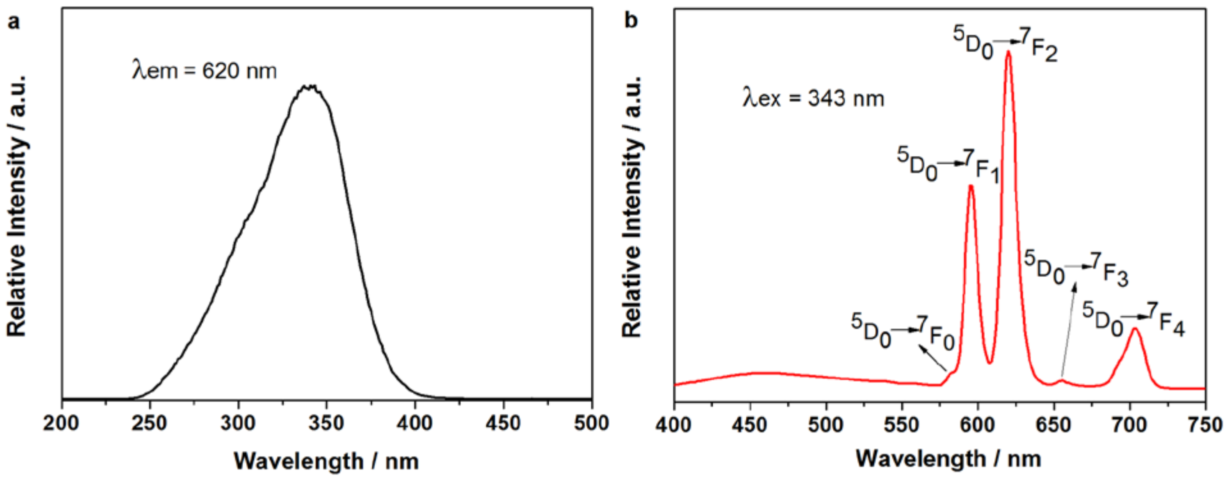


Fig. S4 The excitation(a) and emission (b) spectra of the mesoporous hybrid material Eu(TTA-MSN)$_2$L in aqueous solution (1mg / mL).

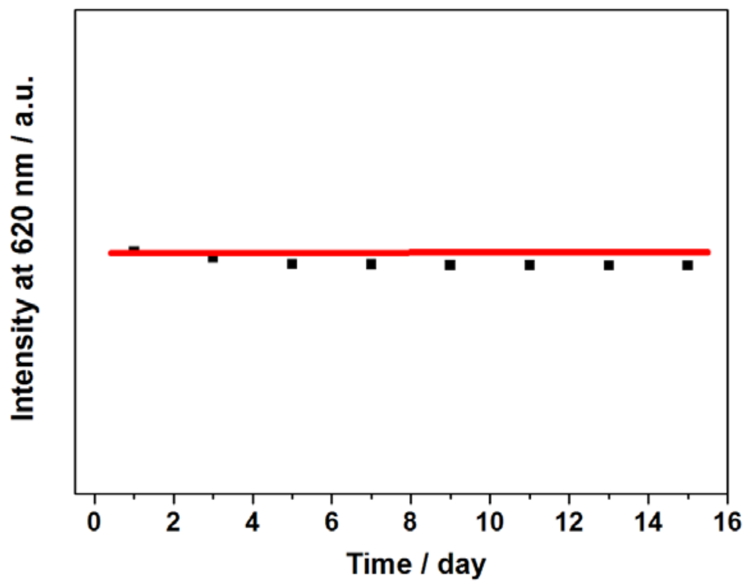


Fig. S5 Day-to day fluorescence stability of Eu(TTA-MSN)$_2$L in aqueous solution.

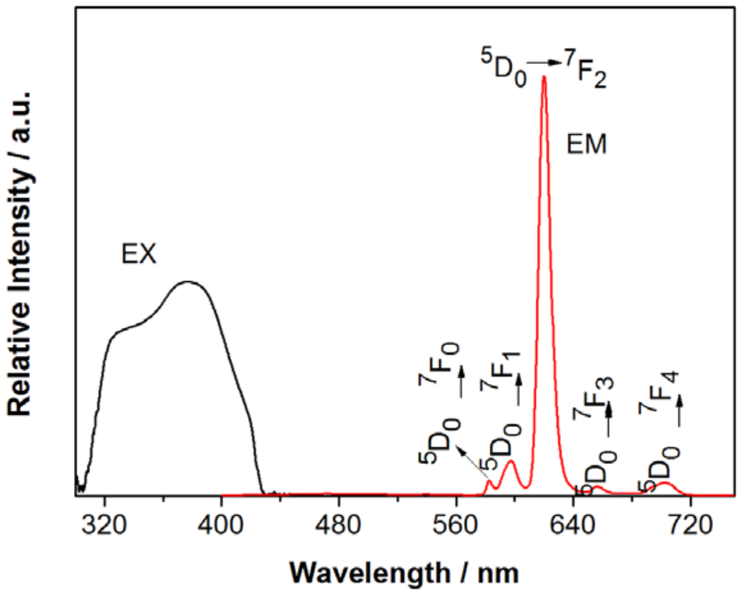


Fig. S6 The excitation (EX) and emission (EM) spectra of the pure Eu(TTA)$_2$L complex.

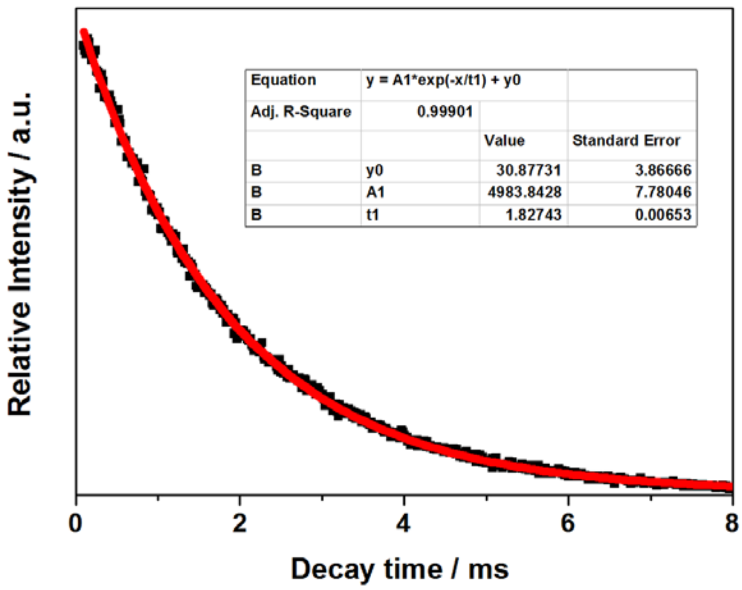


Fig. S7 Luminescence time decay curves for the sample Eu(TTA)$_2$L.

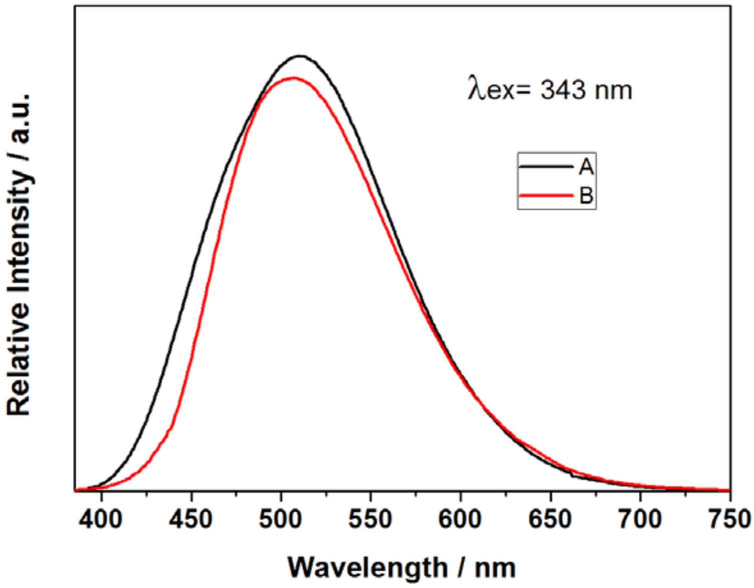


Fig.S8 Emission spectra of Eu(TTA-MSN)$_2$L in aqueous solution solutions (1 mg/mL) upon the addition of Zn^{2+} (2×10^{-4} mol/L) (A) and Emission spectra of Eu(TTA-MSN)$_2$L in aqueous solution solutions (1 mg/mL) upon the addition of Zn^{2+} (2×10^{-4} mol/L) in the presence of other mixture cations (2×10^{-4} mol/L) (B).

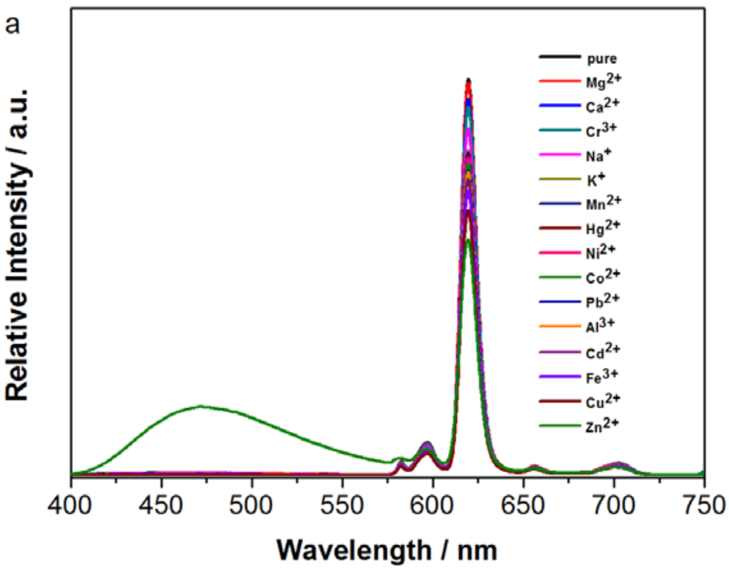


Fig. S9 Emission spectra of Eu(TTA)$_2$L in the aqueous solutions containing different metal ions (1 mg/ mL) when excited at 351 nm.

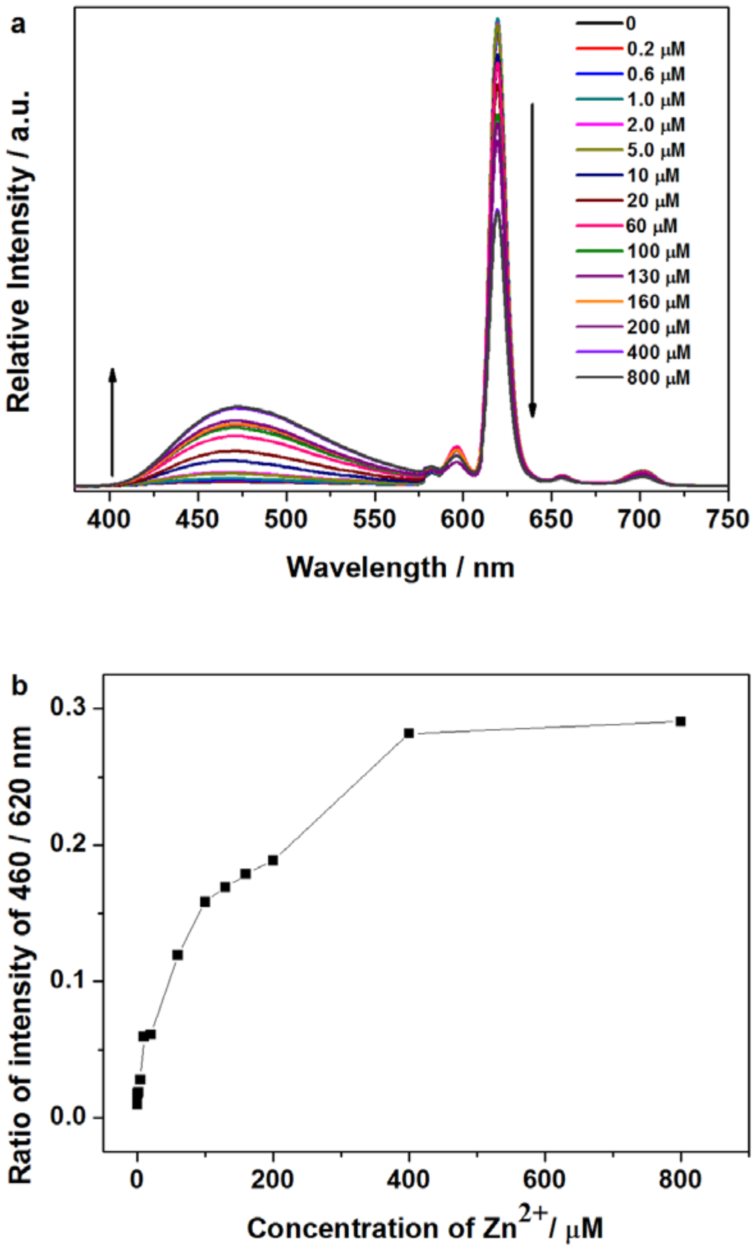


Fig. S10 (a) Photoluminescent spectra of $Eu(TTA)_2L$ in aqueous solutions in the presence of various concentration of Zn^{2+} at an excitation of 371 nm; (b) Ratio of intensity of 472 nm/620 nm of $Eu(TTA)_2L$ in aqueous solutions in the presence of various concentration of Zn^{2+} at an excitation of 371 nm.

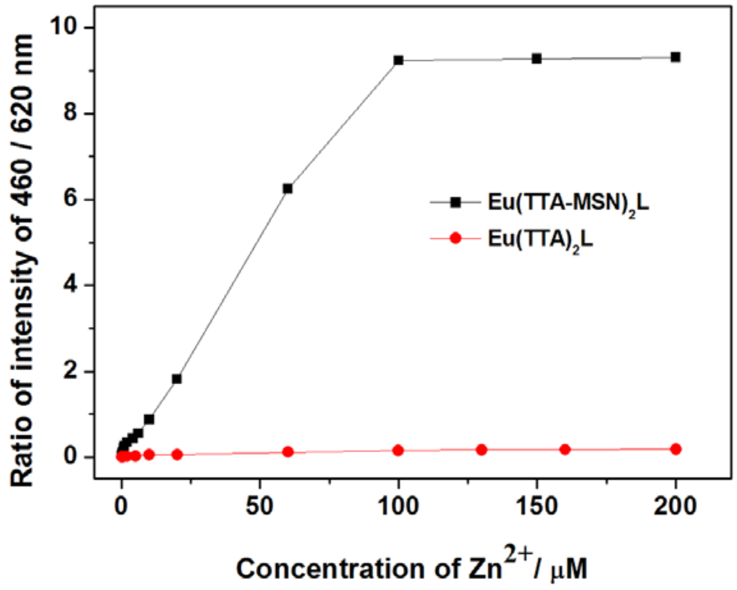


Fig. S11 Ratio of intensity of ligand emission / 620 nm in mesoporous hybrid material Eu(TTA-MSN)$_2$L and Eu(TTA)$_2$L.

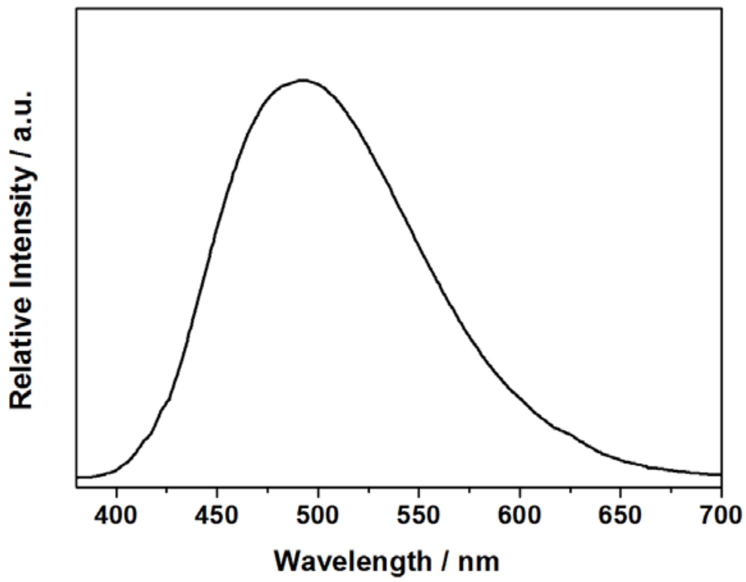


Fig. S12 Emission spectra of Zn^{2+} -centered mesoporous hybrid material Zn(TTA-MSN)L.

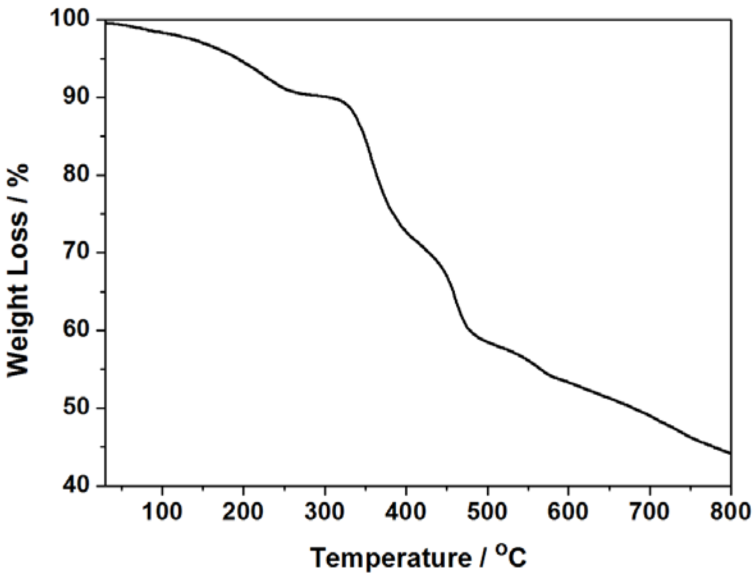


Fig. S13 Thermogravimetry curve of pure complex Eu(TTA)$_2$L.