Supporting Information

Calix[4]arene Derivative Functionalized Lanthanide (Eu, Tb) SBA-15 Mesoporous Hybrids with Covalent Bond: Assembly, Characterization, and Photoluminescence

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^{1}H NMR data for precursors Calix-Si, Calix-NO_2-Si, and Calix-NH_2-Si:

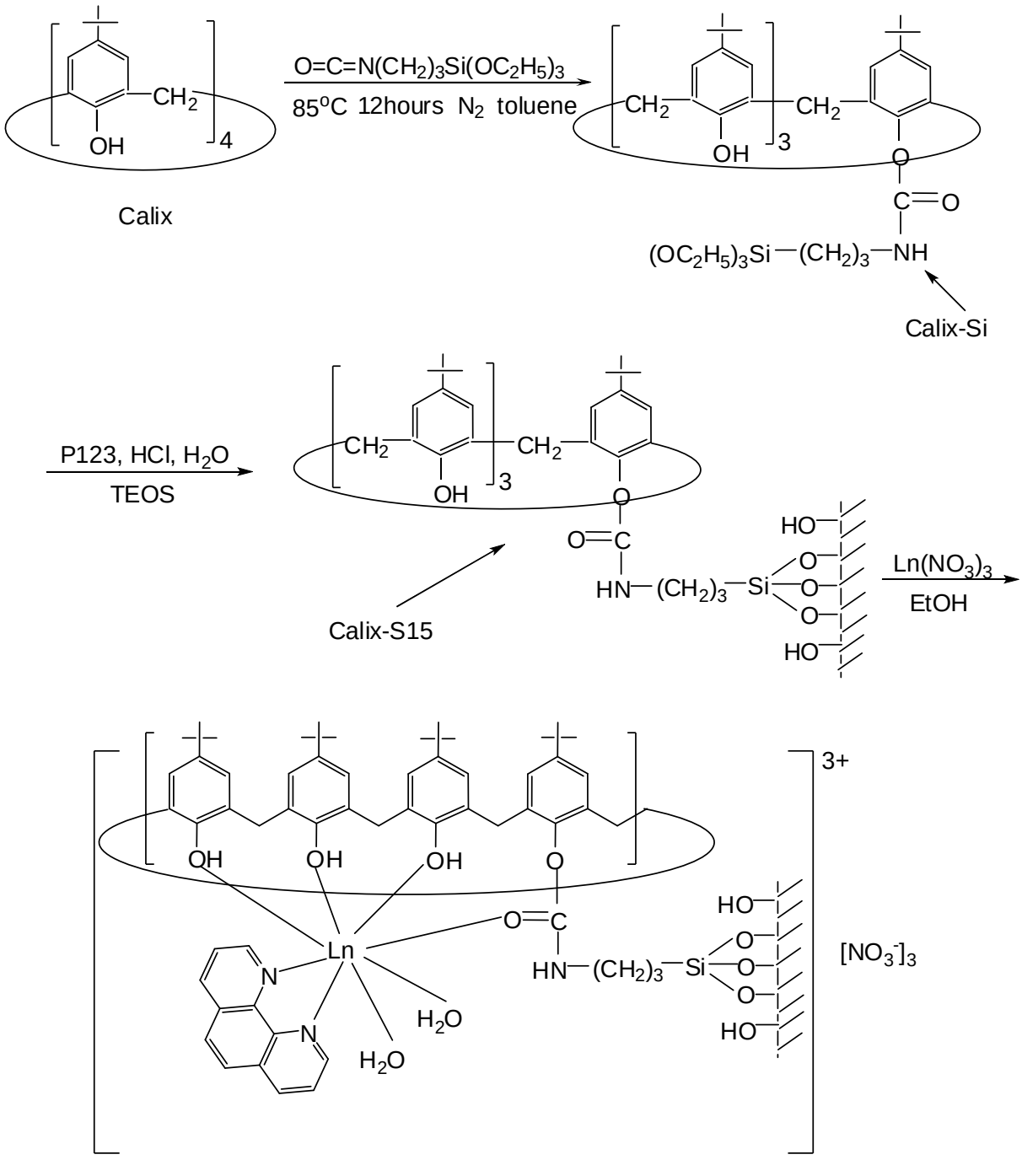
^{1}H NMR for Calix-Si ($CDCl_3$, 400 MHz): δ 0.85-0.87 (2H, t, CH_2), 1.27-1.58 (14H, m, -CH_3, -CH_2), 3.49-3.75 (6H, m, OCH_2), 3.91(m, 2H, -NCH_2), 3.92-4.41(8H, m, Ar-CH_2-Ar), 6.73-7.07 (8H, s, Ar-H), 10.13 (3H, s, Ar-OH). ^{1}H NMR for Calix-NO_2-Si ($CDCl_3$, 400 MHz): 0.67 (2H, t, -CH_2), 0.92(2H, m, -CH_2), 1.28 (9H, t, -CH_3), , 3.19 (2H, m, -NH_2), 3.72-3.77(6H, m. –OCH_2), 3.83-3.85 (8H, m, Ar-CH_2-Ar), 7.41-6.97 (11H, m, Ar-H), 10.21 (3H, s, Ar-OH). ^{1}H NMR for Calix-NH_2-Si ($CDCl_3$, 400 MHz): δ 0.78-0.85 (2H, t), 1.88-1.94 (2H, m), 1.88-1.95(9H, m, -CH_3) 3.54 (2H, m, -$NHCH_2$) , 3.55-3.56(6H, m, -OCH_3), 3.57-3.59 (8H, m, Ar-CH_2-Ar), 6.41-7.07 (11H, m, Ar-H), 10.18 (4H, s, Ar-OH).

(Figure S11 in the below)

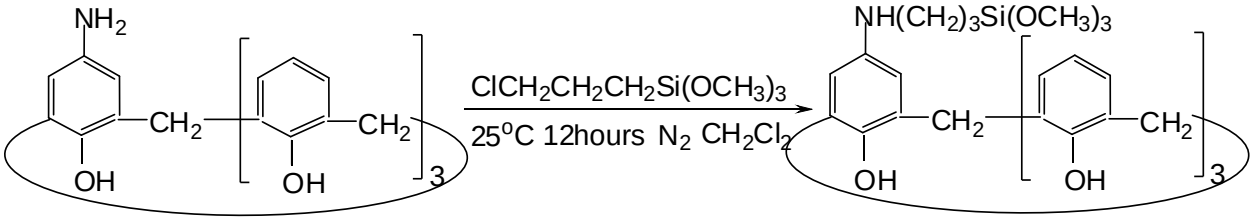
The content of the lanthanide (Eu^{3+}, Tb^{3+}) in the hybrids:

The final hybrids samples are dissolved in nitric acid, then titrated with EDTA solution, using a buffer (*p*H 5.8) and xylenol-orange as indicator. The contents of lanthanide ions (Eu^{3+}, Tb^{3+}) in the hybrids are 7determined by complexometric titrations. For Eu^{3+}, 9.74 % (Eu(Calix-S15)phen), 9.40 % (Eu(Calix-NO_2-S15)phen), 9.51 % (Eu(Calix-NH_2-S15)phen). For Tb^{3+}, 9.63 % (Tb(Calix-S15)phen), 9.26 % (Tb(Calix-NO_2-S15)phen), 9.35 % (Tb(Calix-NH_2-S15)phen). In fact, the sol-gel reaction can not be guaranteed to be completely [1] and so it is difficult to determine the exact composition of the Calix-S15, Calix-NO_2-S15 and Calix-NH_2-S15 networks within the complicated hybrid system not like small molecule complex.

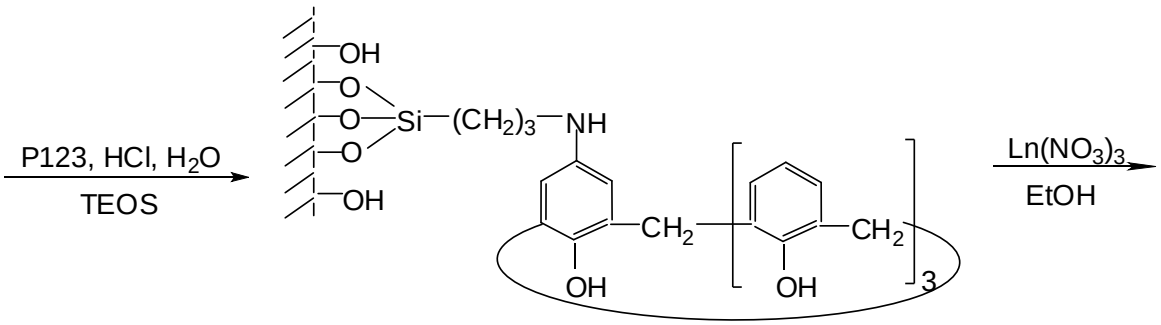
[1] W. S. Kim, M. G. Kim, J. H. Ahn, B. S. Bae, C. B. Park, *Langmuir* **2007**, *23*, 4732-4736; M. C. Goncalves, V. D. Bermudez, R. A. S. Ferreira, L. D. Carlos, D. Ostrovskii, J. Rocha, *Chem. Mater.* **2004**, *16*, 2530-2543.



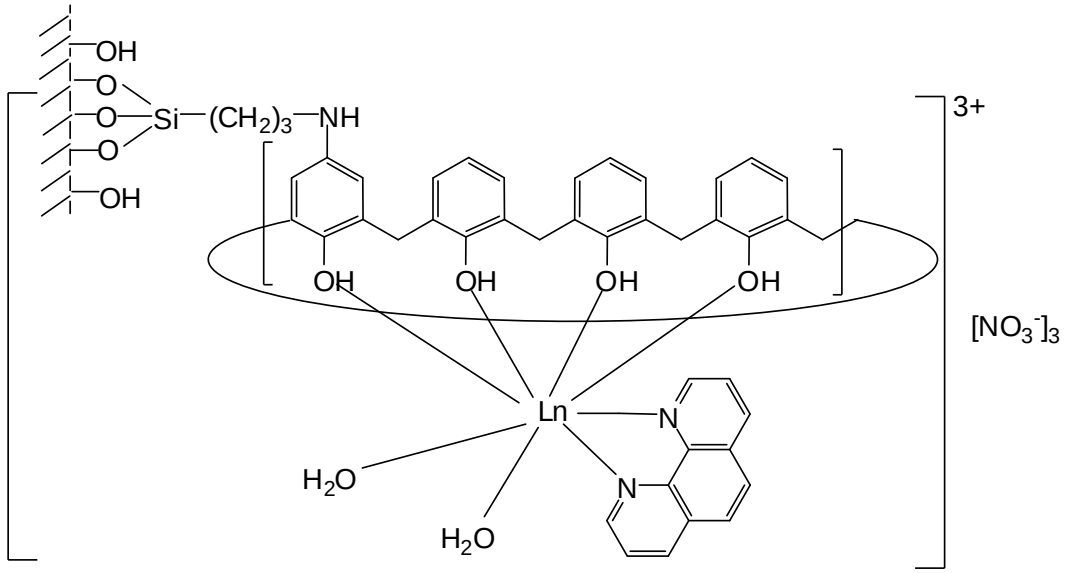
Scheme S1 Synthesis procedure and predicted structure of the ternary mesoporous hybird materials Ln(Calix-S15)phen.



Calix-NH_2 Calix-NH_2-Si



Calix-NH_2-S15



Ln(Calix-NH_2-S15)phen

Scheme S2 Synthesis procedure and predicted structure of the ternary mesoporous hybird materials Ln(Calix-NH_2-S15)phen.

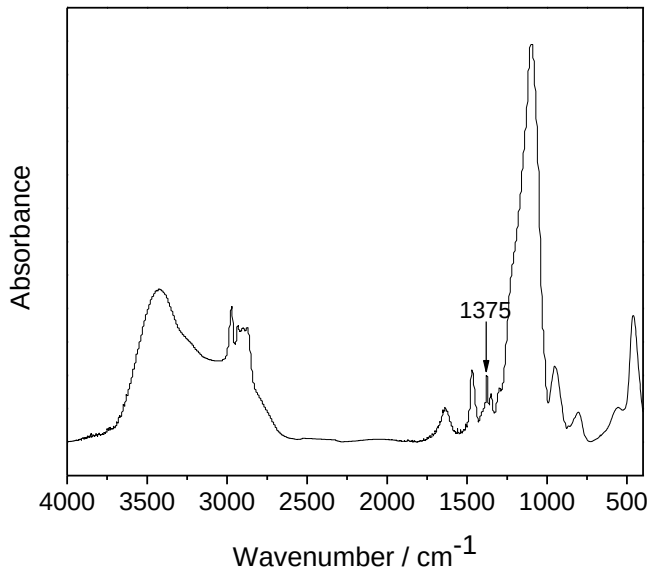


Figure S1 The FTIR spectra of as-synthesized Calix-S15 material.

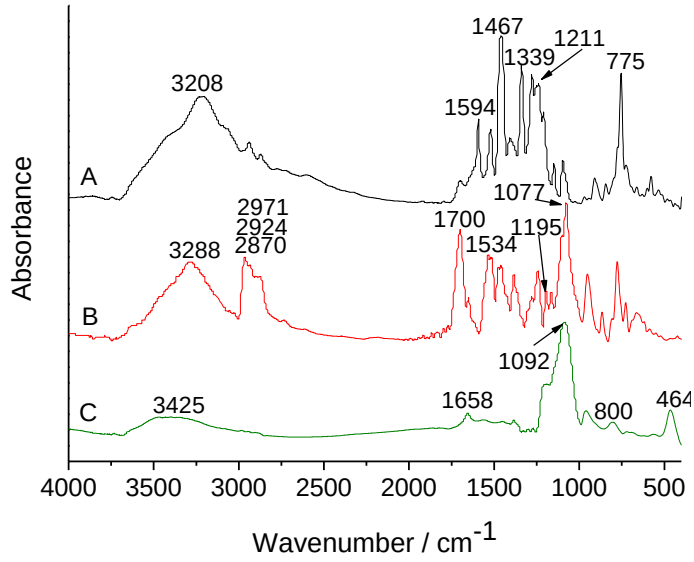


Figure S2(a) The FTIR spectra of Calix (A), the precursor Calix-Si (B) and Calix-functionalized mesoporous hybrid material Calix-S15 (C).

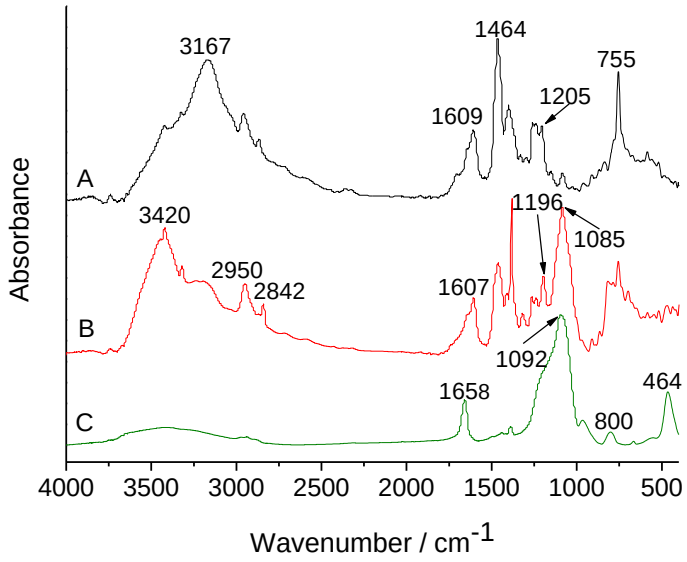


Figure S2(b) The FTIR spectra of Calix-NH_2 (A), the precursor Calix-NH_2-Si (B) and Calix-NO_2-functionalized mesoporous hybrid material Calix-NH_2-S15 (C).

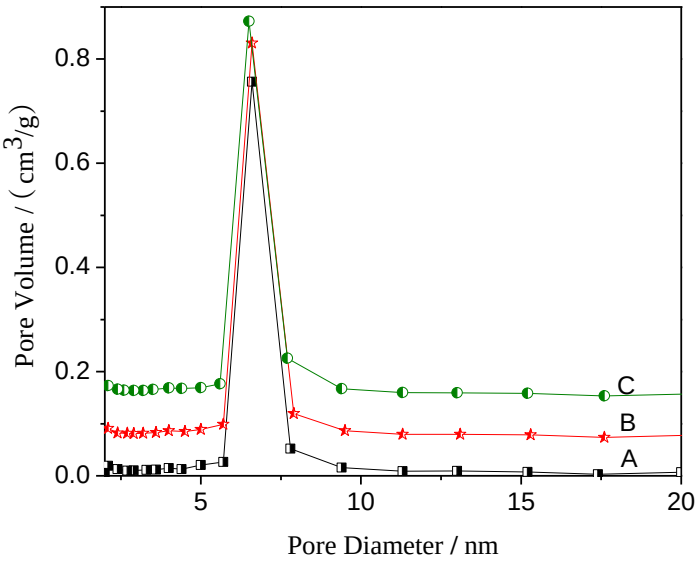


Figure S3 Pore size distribution for calix[4]arene functionalized mesoporous materials Calix-S15 (A), Calix-NO_2-S15 (B), and Calix-NH_2-S15 (C).

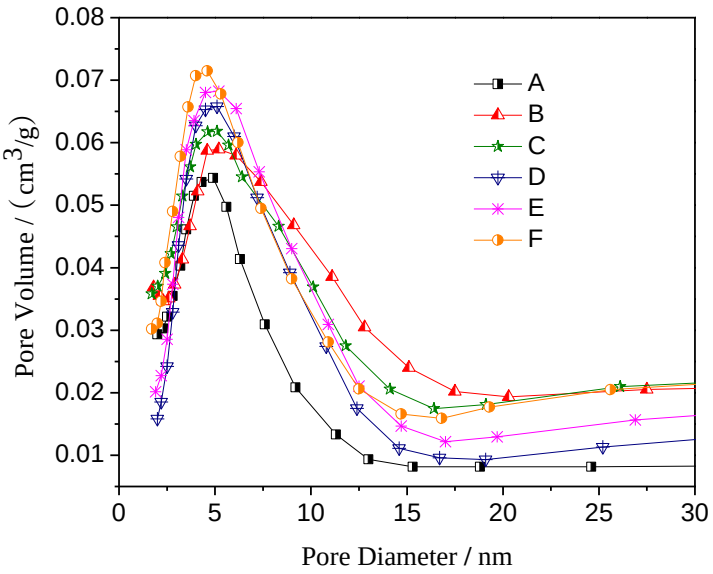


Figure S4 Pore size distributionof ternary lanthanide mesoporous hybrids Eu(Calix-S15)phen (A), Tb(Calix-S15)phen (B), Eu(Calix-NO_2-S15)phen (C), Tb(Calix-NO_2-S15)phen (D), Eu(Calix-NH_2-S15)phen (E), and Tb(Calix-NH_2-S15)phen (F).

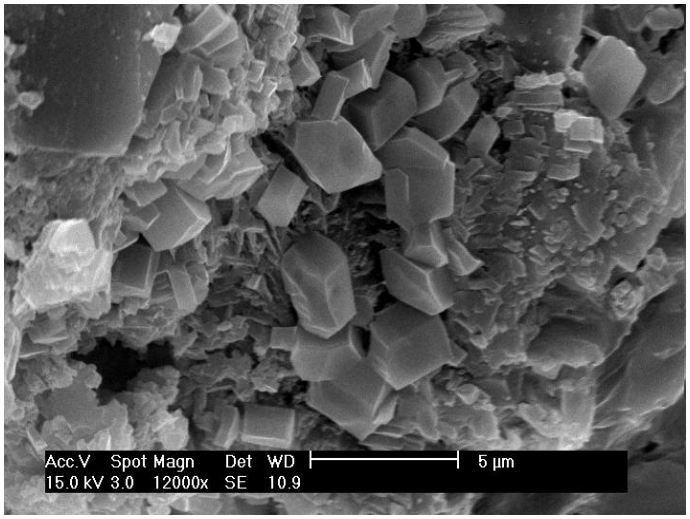


Figure S5 SEM image of ternary mesoporous hybrid Tb(Calix-S15)phen.

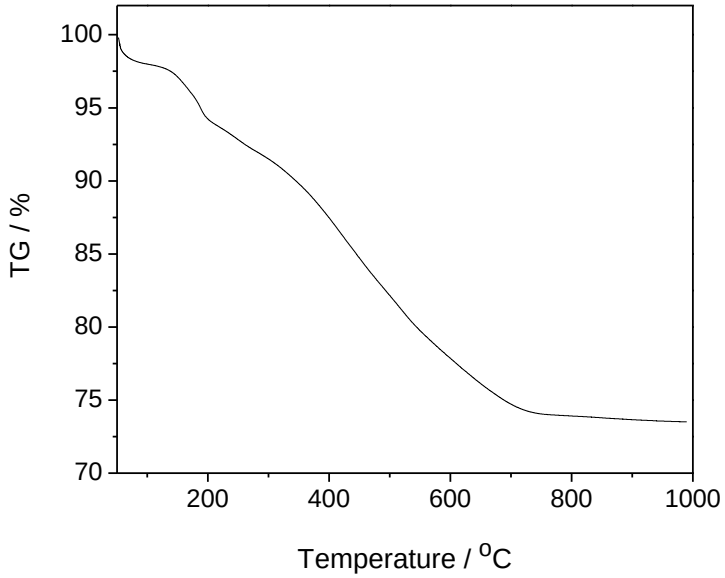


Figure S6 (a) Thermogravimetry trace (TG) of the ternary mesoporous hybrid Tb(Calix-NO_2-S15)phen under oxidizing atmosphere.

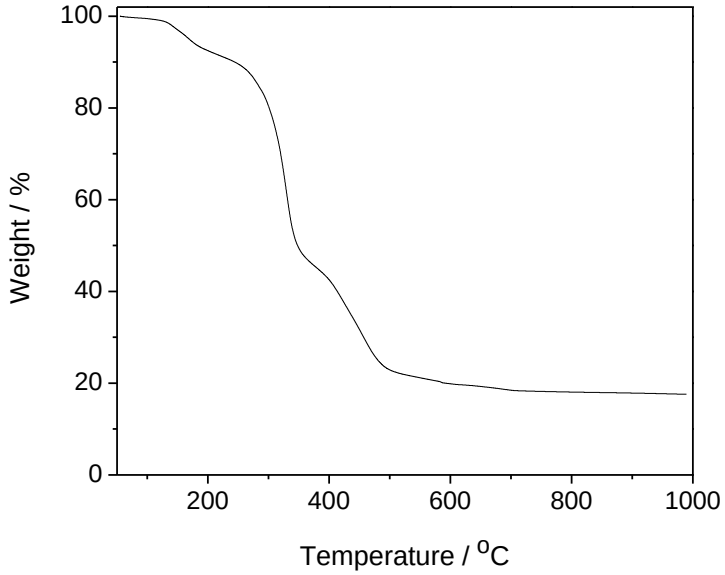


Figure S6 (b) Thermogravimetry trace (TG) of the pure complex Tb(Calix-NO_2)phen.

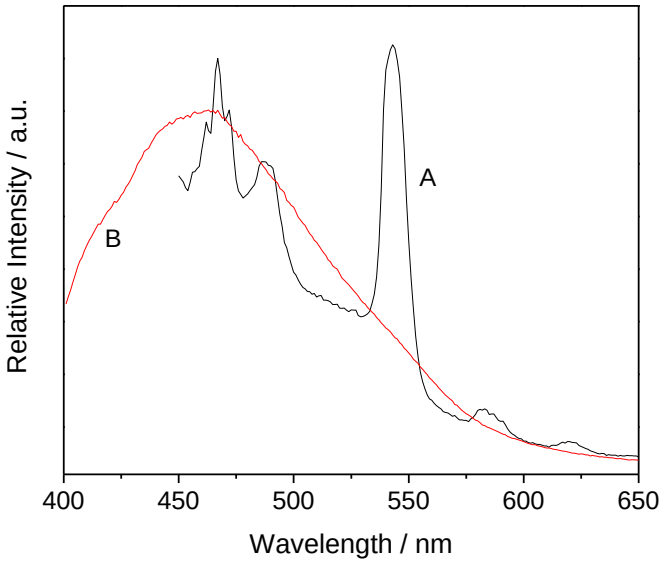


Figure S7 Comparison of normalized luminescence spectra recorded after treatment of the samples at 400 °C in N_2 for 2 hrs (A for Tb(Calix-NO_2-S15)phen and B for Tb(Calix-NO_2)phen).

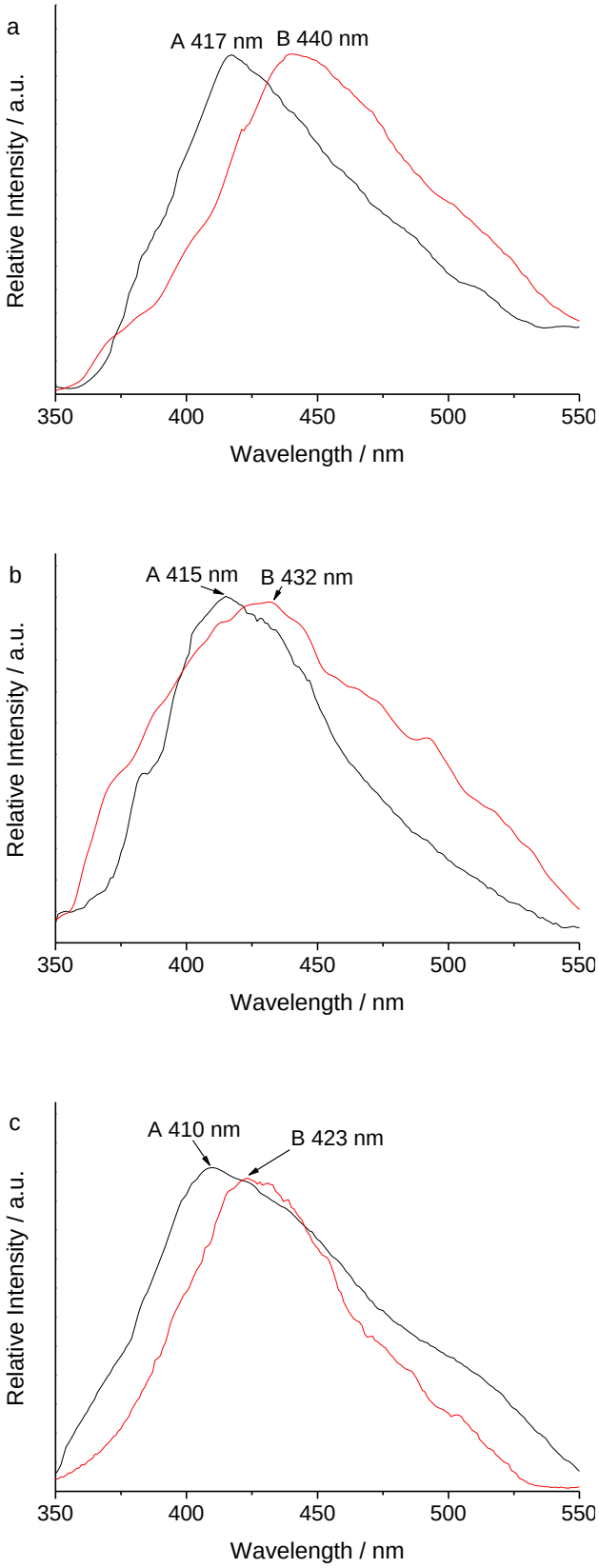
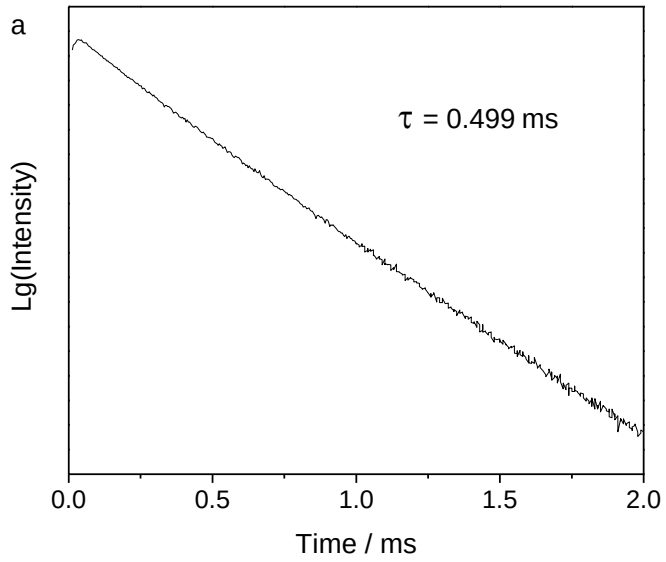
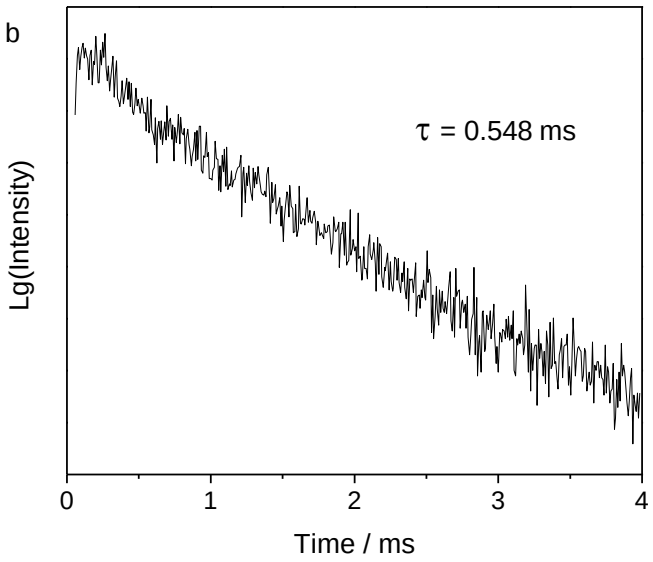


Figure S8 Phosphorescence spectra of (a): Calix (A) and the precursor Calix-Si (B); (b) Calix-NO_2 (A) and the precursor Calix-NO_2-Si(B); (c) Calix-NH_2 (A) and the precursor Calix-NH_2-Si (B).





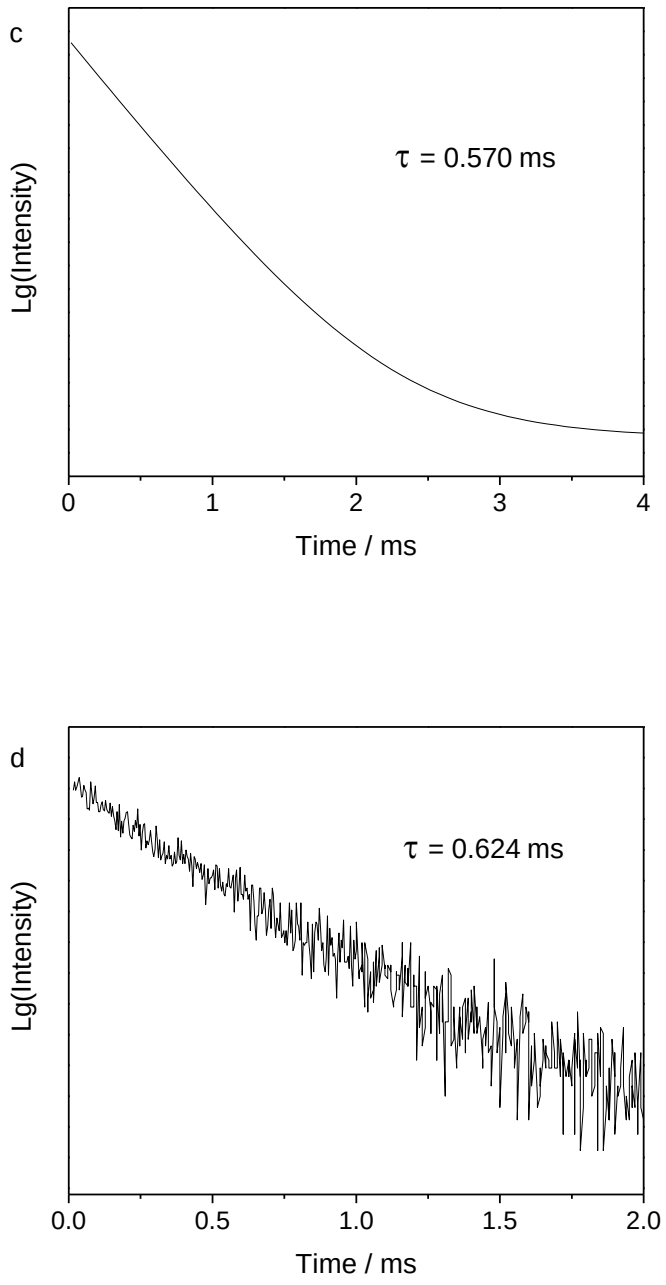
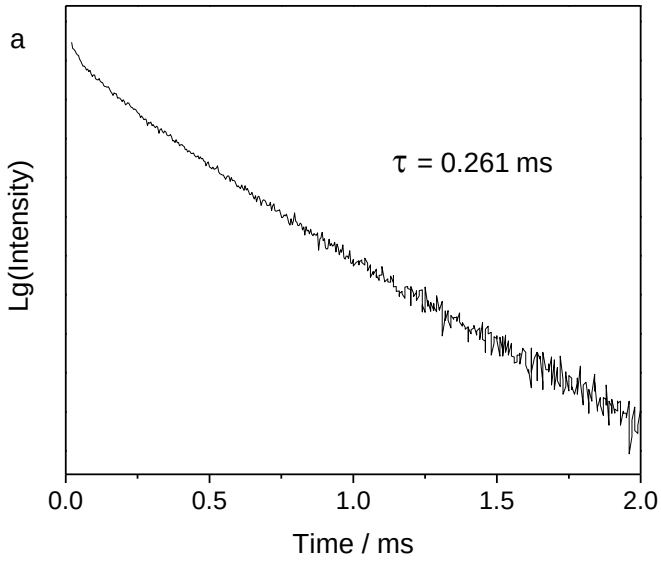
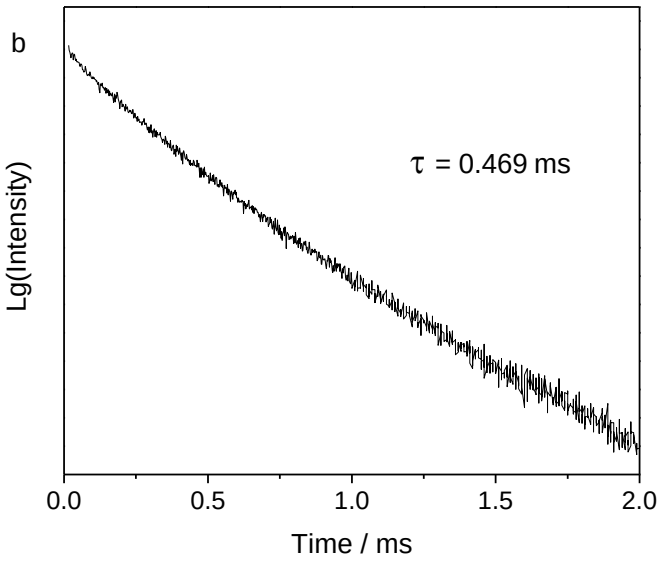


Figure S9 Luminescence decay curve of the Tb-contaning mesoporous hybrid materials: A for Tb(Calix-S15), B for Tb(Calix-NH_2-S15)phen, C for Tb(Calix-NO_2-S15)phen, and D for Tb(Calix-S15)phen.





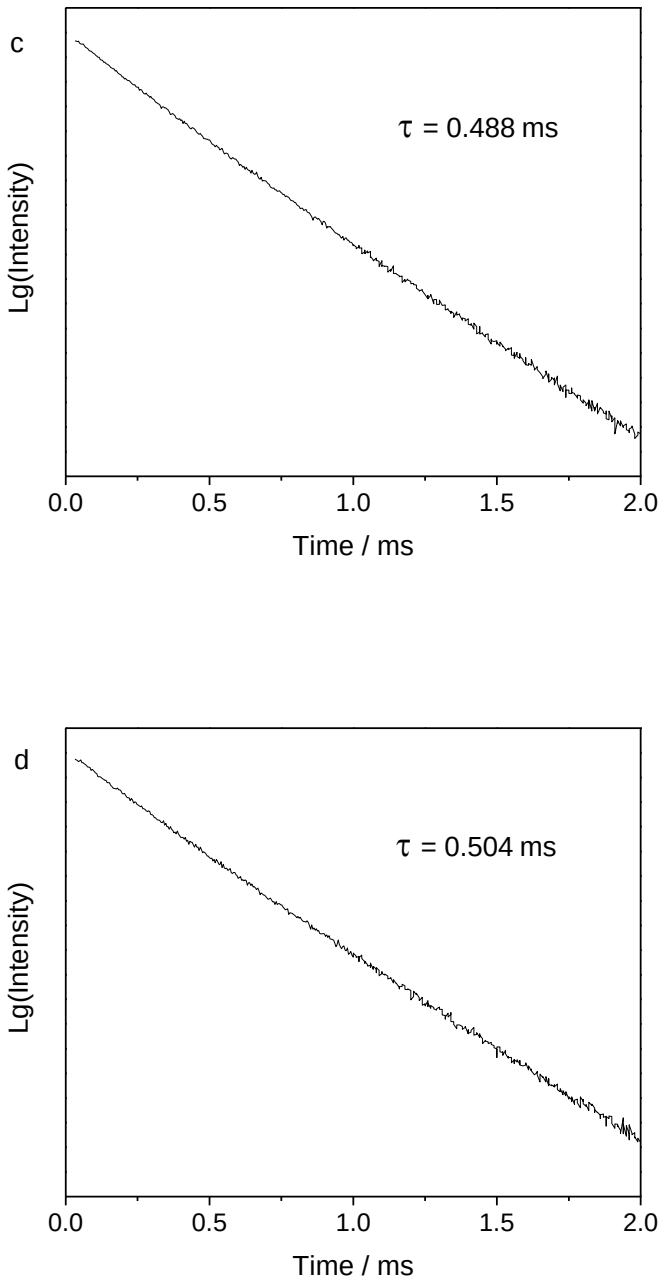


Figure S10 Luminescence decay curve of the Eu-containing mesoporous hybrid materials: A for Eu(Calix-S15), B for Eu(Calix-NH_2-S15)phen, C for Eu(Calix-NO_2-S15)phen, and D for Eu(Calix-S15)phen.

Figure S11 ^{1}H NMR

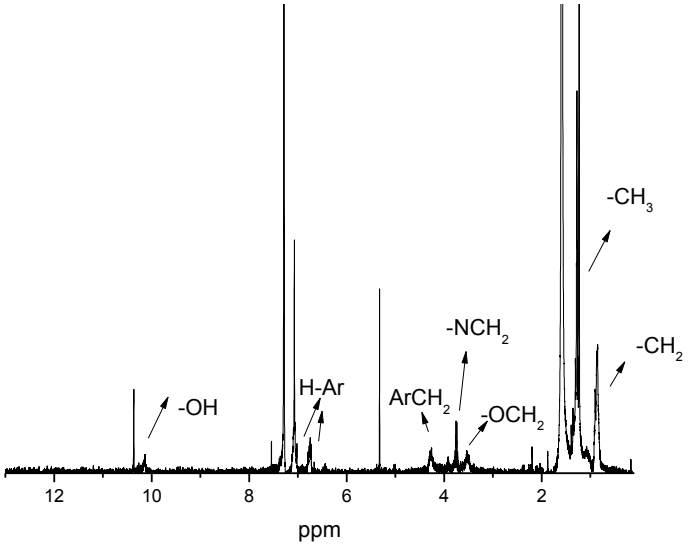


Figure S11 (A) ^{1}H NMR of Calix-Si

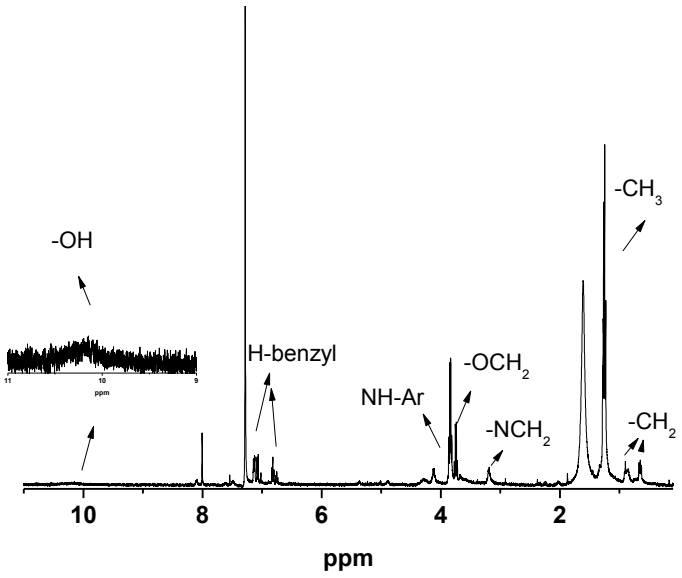


Figure S11 (B) ^{1}H NMR of Calix-NO_2-Si

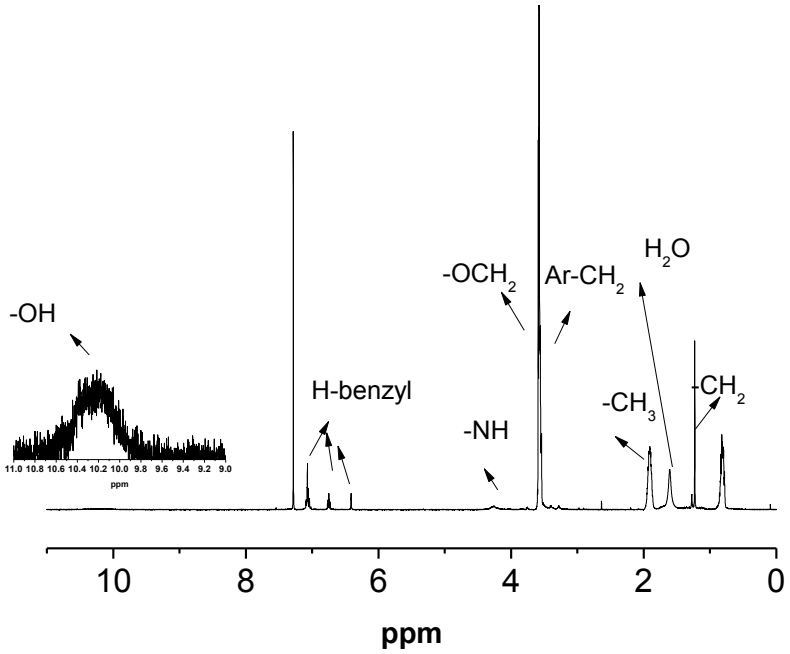


Figure S11 (C) ^{1}H NMR of Calix-NH_2-Si