Chapter 3
Photofunctional Rare Earth Hybrid Materials Based on Organically Modified Mesoporous Silica

Abstract This chapter mainly focuses on recent research progress in photofunctional rare earth hybrid materials based on organically modified mesoporous silica. According to the type of mesoporous host, the content includes photofunctional rare earth hybrid materials based on organically functionalized MCM-type mesoporous silica, organically functionalized SBA-type mesoporous silica, organically functionalized POMs-type mesoporous silica, mesoporous silica composite with inorganic host, and mesoporous silica–polymer composite. Herein, it focuses the research progress of our group.

Keywords Rare earth ion • Photofunctional hybrid materials • Luminescence • Mesoporous silica

3.1 Introduction

Compared to the traditional molecular sieves, mesoporous silica possesses high specific surface area and uniform pore diameter distribution, whose pore diameter is large and can be controlled by means of selecting different templates or adding organic compounds [1, 2]. In the field of host–guest chemistry, mesoporous silica is used as the host for large guest molecules. There are a lot of methods to tune the pore diameter of mesoporous silica, whose basic principle is to reduce or enlarge the size or volume of the micelle of precursors [3, 4]. The free Si–OH groups over the mesoporous materials can undergo the silylation reaction. The surface silylation reaction of mesoporous silica not only can change the surface polarity but also can introduce other functional groups such as mecapto or amino groups. Mesoporous materials have no active center; the low chemical reactivity and high stability limit their applications. In this case, chemical modification of mesoporous silica materials to improve their reactivity has become a hot research topic in recent years. Organic groups interact with the Si–OH group of mesoporous silica to form Si–C or Si–O–C bonds, which realize the functionalization of mesoporous materials and modify the hydrophobicity of the pore wall of mesoporous silica. Subsequently, all kinds of hybrid materials based on mesoporous hosts have been developed [5, 6].

B. Yan, *Photofunctional Rare Earth Hybrid Materials*,
Springer Series in Materials Science 251, DOI 10.1007/978-981-10-2957-8_3

Mesoporous materials are analogous nanomaterials with ordered arrays of uniform nanochannels. They can be used as supports for rare earth complexes [7–19]. MCM-41, one member of the M41S family, possesses regular hexagonal arrays of mesopores, a variable pore diameter of 1.5–30 nm, and tailorable interior surfaces [7–9]. These properties, together with its thermal and mechanical stabilities, make it an ideal host for incorporation of active molecules, so some work has already been devoted to this area [7–9]. SBA-15 has also become a very attractive host because of its high hydrothermal stability and the presence of hexagonally ordered large mesopores (*P*6mm symmetry group) interconnected by complementary micropores. Previous results reveal that the obtained materials possess good luminescence properties and photo and thermal stabilities. The mesoporous silica SBA-16 has also been considered as a good support on account of its three-dimensional structure, consisting of ordered interconnected spherical mesopores, which has a cubic cage-like structure with multidirectional and large pore systems allowing good access for both functionalization and adsorption [10–14]. Periodic mesoporous organosilicas (PMOs) possess some obvious advantages over porous sol–gel-derived or grafted hybrid materials, such as highly ordered structures with very uniform pores, homogeneous distribution of functional groups throughout the whole framework, high loading amount, etc. [15–18].

Up to present, as an important functionalization approach, chemical modification has been extensively utilized in all kinds of materials. The main functionalization method for mesoporous materials is postsynthetic modification. Here only two basic methods are introduced, one is grafting, and the other is co-hydrolysis/polydensation [19, 20]. The grafting method is to link the functional group in the channel of mesoporous host to realize the surface modification of them after the formation of mesoporous structure (generally after removing template). The large amount of Si–OH over the surface of mesoporous silica can behave as the anchor point to graft organic functional groups, [21] and then the organic molecules react with Si–OH to introduce the channels which are grafted onto the surface of mesoporous silica host. The grafting method includes three aspects: inert surface group grafting, active surface group grafting, and position selective grafting, respectively. The removal of templates includes two methods: calcination and extraction. Compared to calcination method, extraction method can retain a great amount of Si–OH groups on the surface, which hardly lose and are easy to graft organic groups. In the grafting modification of mesoporous silica, outside surface is more easily to introduce functional groups than inside surface, and the functionalized groups over outside surface exhibit superior reactivity. So it can selectively functionalize the outside surface of mesoporous silica before removing templates. In order to decrease the reactivity of the groups on outside surface and improve the selectivity of reaction, it can first deactivate the outside surface and then functionalize the inside surface of mesoporous silica. For these functionalized mesoporous silica with grafting method, the organic functional groups possess low loading amount, so it is difficult to control the content and position in the channel, and the distribution in the channel is not uniform. Cohydrolysis/polycondensation belongs to one-step direct synthesis, in which silane sources (cross-linking reagents) are added in the sol to synthesize the mesoporous materials [22, 23]. The functionalization and synthesis of mesoporous silica are processed simultaneously. The advantage of this method to synthesize mesoporous materials is that the organic functional groups distribute in the channels uniformly [24].

For photofunctional mesoporous hybrid materials, considering the requirement of photoactivity, the functionalized units or groups should possess the emissive or absorptive property. Single silane source like cross-linking reagents doesn't have apparent photoactivity, so it needs to be modified with photoactive ligands. In Chap. 2, the corresponding modified path has been discussed, which is important for photofunctional hybrid materials based on organically modified mesoporous silica. On the basis of the above research on rare earth sol–gel-derived hybrid materials with ORMOSILs, it is natural to further attempt the assembly of rare earth mesoporous silica hybrids by grafting rare earth complex units with templates. Novel kinds of rare earth mesoporous hybrid materials, which combine the luminescence properties of rare earth complexes and the particular properties of mesoporous materials, have therefore received considerable attention in recent years. The research has involved many kinds of typical mesoporous hosts such as MCM-41(48), SBA-15(16), periodic mesoporous organosilicas (POMs), etc.

3.2 Photofunctional Rare Earth Hybrid Materials Based on Organically Modified MCM-Type Mesoporous Silica

M41S mesoporous silica family consists of hexagonal crystal system MCM-41, cubic crystal system MCM-48, and layer-like structural MCM-50. Among them, MCM-41 mesoporous silica possesses hexagonal arrangement of one-dimensional channels, which is the most popular system in the M41S family due to its easy synthesis and simple structure. This kind of novel mesoporous materials not only breaks the limit of too small pore diameter of old zeolite materials but also shows the new character such as uniform channel, regular hexagonal or order arrangement, continuous tuning in 2–10 nm range of pore diameter, high specific surface area, good thermal stability, etc. [7–9].

Functionalized mesoporous hybrid materials of photoactive rare earth complexes have appeared in recent decades. The primary research is originated from MCM-41 mesoporous hybrids fabricated with rare earth complexes. There have been extensive studies of the encapsulation and assembly of guest molecules in mesoporous channels [24–44]. Xu et al. study the direct encapsulation of rare earth complexes into MCM-41 host to prepare the hybrid materials, mainly with β-diketonates [24–27]. For example, rare earth complex $[C_5H_5NC_{16}H_{33}][Eu(TTA)_4]$ is incorporated into surface-modified mesoporous molecular sieve Si-MCM-41 via reactions of the surface Si–OH with different silylation agents such as $(C_2H_5O)_3Si(CH_2)_2NH(CH_2)_2NH_2$ (NSED), $(C_2H_5O)_3Si(CH_2)_3NH_2$ (APTES), and $(C_2H_5O)_3Si(CH_2)_3CN$ (TSBT), whose photophysical properties are studied [24].

The results show that the surface silylation of Si-MCM-41 provides a unique chemical environment for the incorporated $[C_5H_5NC_{16}H_{33}][Eu(TTA)_4]$ complex. The content of the rare earth complex in the final products, obtained from chemical analysis, is 6.61% in NSED-Si-MCM-41, 1.84% in APTES-Si-MCM-41, 1.83% in TSBT-Si-MCM-41, and 0.42% in Si-MCM-41, respectively. Hydrogen bonding interactions of the rare earth complex with its surrounding silylating agents alter the photophysical properties of the rare earth complex, whose emission intensity and color purity in these surface-silylated Si-MCM-41 materials increase in the order of Si-MCM-41 < TBST-Si-MCM-41 < APTES-Si-MCM-41 < NSED-Si-MCM-41. Because of the strongest hydrogen bonding in NSED-Si-MCM-41, the rare earth complex only emits light with a single wavelength, corresponding to $^5D_0$-$^7F_2$, which is rarely seen in the luminescence of rare earth complexes. Similarly, considering the suitable match between the pore diameter of MCM-41 host and the size of rare earth complex guest, the other rare earth β-diketonates can also be introduced to assembly the hybrid materials [25–27].

Besides, Carlos's group also study the MCM-41 hybrid materials with special pyrazolylpyridine-derived ORMOSIL linkage [28–31]. Gago et al. use mesoporous silica MCM-41 functionalized with a chelating pyrazolylpyridine ligand (MCM-41-L2) (L2 = (3-triethoxysilylpropyl)[3-(2-pyridyl)-1-pyrazolyl] acetamide) as a support for the immobilization of tris(*β*-diketonate) complexes $RE(NTA)_3$ (RE = Eu, Gd; NTA = 1-(2-naphthoyl)-3,3,3-trifluoroacetone) [28]. The spectroscopic studies supported by ab initio calculations evident that the immobilized Eu^{3+} complex is an eight-coordinate with a local coordination environment similar to that for a model complex containing ethyl[3-(2-pyridyl)-1-pyrazolyl]acetate (L1). No emission from the pyrazolylpyridine ligands is observed in the room-temperature emission spectrum of MCM-41-L2/Eu in spite of only about one-third engaged in coordination with Eu^{3+} ions, while the pyrazolylpyridine groups in the precursor ligand–silica can exhibit efficient emission. Furthermore, the radiance value measured for MCM-41-L2/Eu ($0.33\ \mu W\cdot cm^{-2}$) is only about one-half of that measured for the complex $Eu(NTA)_3\cdot L1$ ($0.73\ \mu W\cdot cm^{-2}$), even though the concentration of emitting centers in the MCM material is much lower, which suggests the existence of an unusual two-step intermolecular energy transfer between "free" and "coordinated" ligands in MCM-41-L2/Eu to culminate in the observation of enhanced Eu^{3+} luminescence. Bruno et al. prepare hybrid ligand–silica by reaction of the ordered mesoporous silica MCM-41 with 3-triethoxysilylpropyl 4-pyridylacetamide (L3) [29]. Elemental analysis indicates a pyridyl group loading of $0.93\ mmolg^{-1}$. Pyridyl-functionalized MCM-41(L3) is treated with chloroform solutions of rare earth tris-β-diketonate complexes $Ln(NTA)_3(H_2O)_2$ (RE = Eu, Gd) to give the surface-bound monosubstituted species $Ln(NTA)_3(H_2O)(L3)$, whose residual coordinated water molecules are subsequently replaced by pyridine (py) or methyl phenyl sulfoxide (mpso) to give immobilized $RE(NTA)_3(py)(L)$ and $RE(NTA)_3(mpso)(L3)$ species. Variation of the excitation wavelength confirms that all of the Eu^{3+} occupies the same average local environment within each sample. The interaction between the host and guest has a strong effect on the excited states of the organic ligands. They further investigate a luminescent hybrid material by impregnating the Eu^{3+} β-diketonate complex $Eu(NTA)_3L0$ within the channels of MCM-41 (L0 = 2-(3(5)-pyrazolyl)pyridine) [30]. The low- (14 K) and room-temperature emission spectra of the Eu-modified mesoporous material display the typical Eu^{3+} intra-$4f^6$ lines, whose $^5D_0$ quantum efficiency is estimated to be 21.1%, which is lower than 46.1% for the model complex $Eu(NTA)_3L0$. This difference is ascribed to the presence of an excited state of the organic ligands in the MCM-41, which lies approximately resonant with the $^5D_1$ intra-$4f^6$ level to open up an additional non-radiative channel.

Recently, Felício et al. directly prepare MCM-41 hybrids incorporated with $Eu(TTA)_3$ephen [31]. The combination of UV–Vis and photoluminescence spectroscopy shows that the complex incorporation seems to modify essentially the second Eu^{3+} coordination shell. The impregnated hybrid material shows maximum $^5D_0$ quantum yield value of 0.31, which is almost in the same scale as covalently bonded one. To deeply understand the photoluminescence process, the ligand-to-Eu^{3+} intramolecular energy transfer and back-transfer rates are also predicted, which are in good agreement. The dominant pathway involves the energy transfer between the lowest energy ligand triplet and the $^5D_0$ level (9.70×10^7 s^{-1}).

Zhang's group study MCM-41-based hybrids with pyridine derivative linkages in detail [32–34]. Firstly, Li et al. prepare organo-functionalized MCM-41 containing non-covalently linked 1,10-phenanthroline (phen-MCM-41) [32]. The one-step synthesis presents an alternative to postsynthesis grafting methods. The high affinity toward various cations and the blue emission of the modified phenanthroline that is proven to be within the channel renders phen-MCM-41a promising candidate both for optical devices and the removal of anions. The desired properties of MCM-41 can be tailored by an appropriate choice of the precursors and the metal ions. Their emphasis has been on NIR-luminescent mesoporous hybrids [33, 34]. For instance, Sun et al. prepare NIR-luminescent mesoporous materials by linking ternary rare earth (Er^{3+}, Nd^{3+}, Yb^{3+}, Sm^{3+}, Pr^{3+}) complexes to MCM-41 through a functionalized phen group, 5-[*N*,*N*-bis-3-(triethoxysilyl)propyl] ureyl-1,10-phenanthroline on the basis of Li's work. Here, two β-diketonates HFTH (4,4,5,5,6,6,6-heptafluoro-1-(2-thienyl)hexane-1,3-dionate and TFNB (4,4,4-trifluoro-1-(2-naphthyl)-1,3-butanedione) are used as the second ligands [33]. Upon excitation at the absorption wavelength of the organic ligands, all these materials show the characteristic NIR luminescence of the corresponding rare earth ions. They further prepare mesoporous hybrid material, Q-MCM-41 based on a bifunctional ligand, 8-hydroxyquinoline-functionalized organosilane (Q-Si) [34]. Furthermore, through ligand exchange reactions, new NIR-luminescent mesoporous REQ_3-MCM-41 (RE = Er, Nd, Yb) materials are prepared by linking rare earth quinolinate complexes to Q-MCM-41. In addition, Feng et al. focus on the Tm mesoporous MCM-41 hybrid materials. Still using phen-Si as linkage, they prepare three NIR-luminescent thulium complexes covalently bonded to the ordered mesoporous material MCM-41 ($Tm(L)_3$phen–MCM-41 (L = TTA, TFNB, DBM)] [36, 37]. The full widths at half maximum (fwhm) of the 1474 nm emission band are 96 nm, 100 nm, and 110 nm for $Tm(TTA)_3$phen–MCM-41, $Tm(TFNB)_3$phen–MCM-41,

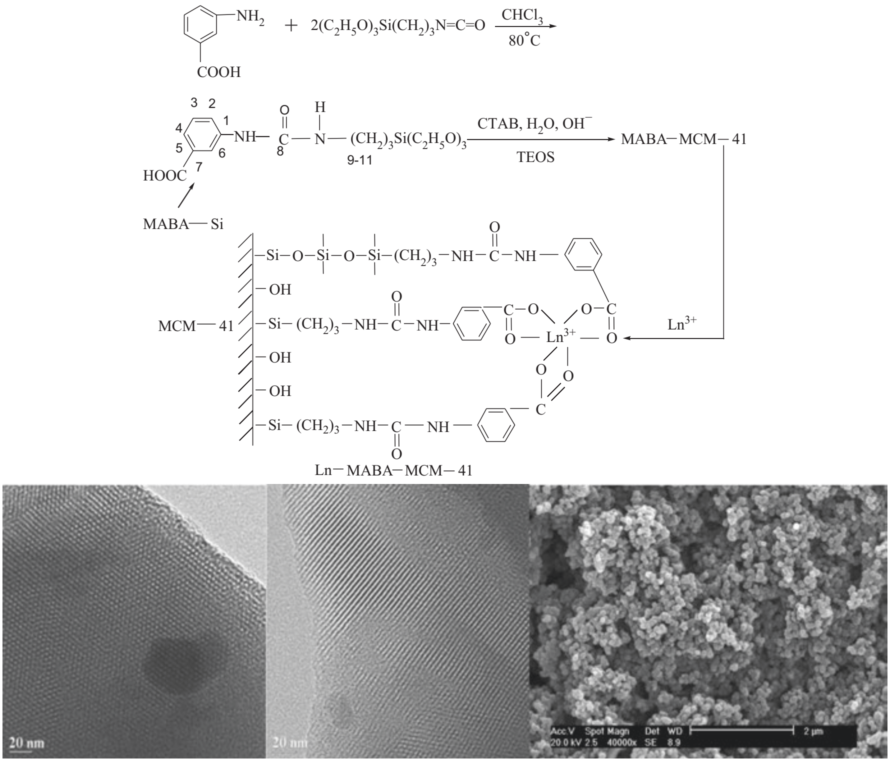

Fig. 3.1 The scheme for synthesis procedure and predicted structure of RE-MABA-MCM-41(RE = Tb, Eu) (*Top*); selected HRTEM recorded along the [100], [110] zone axes (left, middle) and SEM image (*Right*) of Tb-MABA-MCM-41 (*Bottom*) (Reprinted with permission from Ref. [39]. Copyright 2010, Elsevier Publisher Ltd)

and Tm(DBM)$_3$phen-MCM-41, respectively. The good luminescent performances enable these materials to have potential applications in optical amplification (broadening amplification band from C band (1530–1560 nm) to S* band (1450–1500 nm)).

Yan's group has also prepare some rare earth mesoporous hybrids of MCM-41 hosts based on their previous work on the ORMOSILs introduced in Chap. 2 [37–44]. Li et al. prepare a series of aromatic carboxylic acids (with amino, hydroxyl, and methyl substituted groups) grafted ORMOSILs modified MCM-41 hybrid materials through the different modification paths [37–39]. Here, an example is given for the aminobenzoic acid grafted ORMOSILs modified MCM-41 hybrid materials. The rare earth (Tb^{3+}, Eu^{3+}) complexes are covalently immobilized in MCM-41 through the modification of MBA (*meta*-aminobenzoic acid) with TESPIC, using a co-condensation method (Fig. 3.1 (Top)) [39]. The final luminescent mesoporous materials have high surface area, uniformity in the mesopore structure, and good crystallinity. The HTEM images (Fig. 3.1(Bottom) left and middle)) of

Tb-MABA-MCM-41 suggest that the ordered pore structure is still substantially conserved after the complexation, which shows *p*6*mm* symmetry and well-ordered hexagonal structure in agreement with the SAXRD and N_2 adsorption/desorption isotherms. The distance between the centers of the mesopore is estimated to be 3.91 nm, which is in good agreement with the value determined from the corresponding XRD data. Moreover, Tb-MABA-MCM-41 exhibits the stronger characteristic emission of Tb^{3+} and longer lifetime than Eu-MABA-MCM-41. Compared with pure $Tb(MABA)_3$ complex, the increase of luminescence intensity in Tb-MABA-MCM-41 shows that the mesoporous MCM-41 is an excellent host for the luminescence $Tb(MABA)_3$ complex. Similarly, other kinds of aromatic carboxylic acid ligands can be grafted onto an MCM-41 host [39, 40].

MCM-41 materials directly covalently bonded with modified β-diketones have also been obtained [41–43]. Zhou et al. report MCM-41 mesoporous hybrids with dibenzoylmethane (DBM) and acetylacetone (ACAC) ORMOSILs [40]. The hybrid materials with covalently bonded MCM-41 have higher intensities and longer lifetimes than those of pure complexes (Eu-DBM and Tb-ACAC), suggesting that covalently bonded MCM-41 host can decrease the concentration quenching effect and enhance the luminescent stability. Moreover, the luminescence properties of mesoporous hybrids are comparable to those of sol–gel-derived hybrids with the same ORMOSILs (TTA-Si) [41]. In addition, Li et al. functionalize MCM-41 mesoporous silica with two kinds of macrocyclic calixarene derivatives Calix [4] and Calix [4]Br (Calix [4] = P-tert-butylcalix[4]arene, Calix [4]Br = 5,11,17,23-tetra-tert-butyl-25,27-bihydroxy-26,28-bibromopropoxycalix[4]arene) [43]. More recently, Gu et al. report the synthesis of organic ligands (9-hydroxyphenalenone (HPO), 2-methyl-9-hydroxyphenalenone (MHPO), 6-hydroxybenz[de]anthracen-7-one (HBAO)) and their assembly with phen-Si-functionalized mesoporous MCM-41 to obtain the ternary Eu^{3+} hybrid materials, EuL_3phen-MCM-41 (L = HPO, MHPO, HBAO) [44]. It is worth noting that the excitation spectra of these hybrid materials have a broad absorption, which occupies from UV to visible region (250–475 nm) consisting of two absorption centers from phen-MCM-41 and three ligands (HPO, MHPO, HBAO), respectively. Upon ligand-mediated excitation with the visible light, the low efficient energy transfer occurs between the organic ligands and europium(III) ion under visible excitation, but the maximum wavelength (456 nm/457 nm/451 nm) locates at blue light region, which is in consistent with the blue LED light. Then this hybrid material may be a feasible alternative in producing time-resolved luminescence under LED excitation.

Besides MCM-41 hybrids, Meng et al. report the studies on functionalized MCM-48 mesoporous hybrids with europium β-diketonate complexes ($Eu(DBM)_3·2H_2O$) using a simple wet impregnation method [44, 45]. MCM-48 has a very high surface area, large pore volume, and narrow pore size distribution, adjustable in the 1.5–10 nm range. The high surface area exhibited by MCM-48 makes it an attractive host for the insertion of large amounts of bulky molecules with functional properties. Shifts in the absorption maxima are observed in the excitation spectra, which is in relation to host–guest interactions between the organic complex and the silica matrix. The role of the O^{2-}–Eu^{3+} charge-transfer band and the impact of silylation on the luminescence properties at room and high temperatures are demonstrated.

3.3 Photofunctional Rare Earth Hybrid Materials Based on Organically Modified SBA-Type Mesoporous Silica

SBA series belongs to mesoporous silica materials containing cage structures, which is synthesized in strong acidic condition using double-chain surfactant as template. Among the series, the most important system is pure mesoporous silica material SBA-15 with hexagonal structure (P6mm), prepared using special hydrophilic tri-block copolymer (poly (oxyethylene)-poly (oxypropylene)-poly (oxyethylene) (PEO-PPO-PEO) as template. Besides, another SBA-16 mesoporous silica material with cubic cage structure can be synthesized using large PEO chain block copolymer [10–14].

There are many reports on photofunctional rare earth SBA-15 mesoporous hybrids [46–61]. Zhang's group concentrate on SBA-15-type hybrid materials with ORMOSILs derived from pyridine derivatives (bpy, phen, etc.) as the first ligand and second ligand such as β-diketones (DBM, HFTH, TFNB) [46, 47]. In Peng et al.'s work on phen-Si modified SBA-15 hybrids (Eu(TTA)3phen-SBA-15) [47], and they confirm that these chemically bonded mesoporous hybrids show more favorable luminescence performances than the corresponding doped systems. The thermal stability of the rare earth complex is also evidently improved. Corriu et al. prepare ordered mesoporous silica containing 3-chloropropyl groups by a direct synthetic approach [48]. Nucleophilic displacement of chloro groups by cyclam moieties (cyclam = 1,4,8,11-tetraazacyclotetradecane) is then achieved almost quantitatively. Subsequent treatment of solids containing different amounts of cyclam moieties with an ethanolic solution of Eu^{3+} chloride gives rise to 1:1 EuIII/cyclam complexes. The EXAFS studies have shown that Eu(III) adopts an octahedral geometry.

Besides, Sun et al. prepare the dual–functional ligand Q-Si and the mesoporous hybrid material REQ_3-SBA-15 (Q = 8-hydroxyquinoline; RE = Er, Nd, Yb) (Fig. 3.2) [49]. After ligand-mediated excitation, all of the emission spectra of the LnQ_3-SBA-15 materials show the characteristic NIR luminescence of the corresponding rare earth ions. As both the organic ligands and the emission of the rare earth ions can be tuned, a variety of mesoporous materials exhibiting a wide range of optical properties can be envisaged useful for optical applications. Besides, they further realize the attachment of ternary rare earth complexes ($RE(HFTH)_3phen$) (RE = Er, Nd, Yb, Sm) and ($Pr(TFNB)_3phen$) to the ordered SBA-15 mesoporous materials via a functionalized phen-Si linker, all of which also display the characteristic NIR luminescence of the corresponding RE^{3+} ions [50]. Based on their work on visible-luminescent SBA-15 mesoporous hybrids, it can be expected that the luminescence

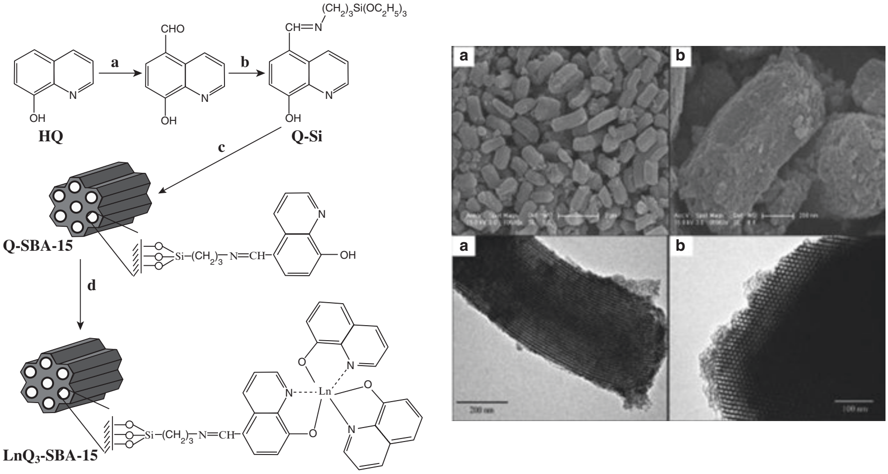

Fig. 3.2 The scheme for synthesis procedure and predicted structure of REQ$_3$-SBA-15 (RE = Nd, Er, Yb) hybrids (*Left*); SEM images of surfactant-extracted Q-SBA-15 material (*middle*) and TEM images of surfactant-extracted Q-SBA-15 material along the [110] (*a*) and [100] (*b*) zone axes (*Right*) (Reprinted with permission from [49]. Copyright 2008, The American Chemical Society)

spectral region from 1300 to 1600 nm is of particular interest for telecommunications applications.

Yan's group also study the functionalized SBA-15 mesoporous host with ORMOSILs derived from different organic precursors, including β-diketones (1-(2-naphthoyl)-3,3,3-trifluoroacetone (NTA), TTA, DBM, ACAC, calixarene derivatives (Calix, Calix-NH$_2$, Calix-NO$_2$), aromatic carboxylic acids, and sulfoxide ligands (oxobenzyldimethyl sulfoxide, benzylsulfinylacetylbenzene, porphyrin and hydroxyphenalen-1-one derivatives, etc.) [51–61]. They all have high surface areas and uniform mesostructures and crystallinities. The efficient intramolecular energy transfer in mesoporous materials mainly occurs between the modified ligand and the central RE^{3+} ion. For example, Li et al. prepare mesoporous hybrid materials by linking the binary and ternary Eu^{3+} complexes to the functionalized ordered mesoporous SBA-15 with the modified 1-(2-naphthoyl)-3,3,3-trifluoroacetone (NTA) (Fig. 3.3) [51]. Among these, Eu(NTA-SBA-15)$_3$bpy exhibited the characteristic emission of Eu^{3+} ion under UV irradiation with higher $^5D_0$ luminescence quantum efficiency than the pure Eu(NTA)$_3$bpy complex and other hybrid materials. This work can be extended to other β-diketone-grafted ORMOSIL-modified SBA-15 hybrid materials [52–56]. Li et al. synthesize the mesoporous hybrid materials phen-RE(OBDS)$_3$-SBA-15 and phen-RE(BSAB)$_3$-SBA-15 (RE = Eu, Tb) by linking the ternary rare earth (Eu^{3+}, Tb^{3+}) complexes to the functionalized ordered mesoporous SBA-15 with the modified sulfoxide (OBDS–Si and BSAB–Si) [57]. The resulted mesoporous hybrids exhibit a strong, nearly monochromatic emission of Eu^{3+} ions, and good thermal stability. Li et al. prepare three types of ternary rare earth mesoporous hybrid materials ((RE(Calix-S15)phen, RE(Calix-NO$_2$-S15)

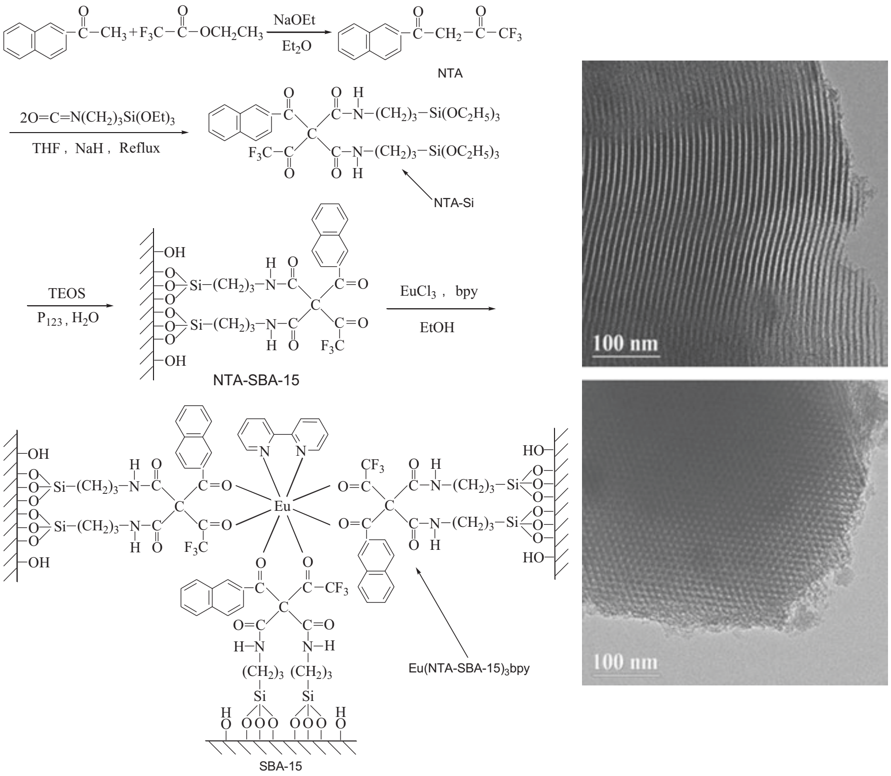

Fig. 3.3 Scheme of the synthesis process of NTA–Si and predicted structure of hybrid mesoporous material Eu(NTA-SBA-15)$_3$bpy (*Left*); and HRTEM images of Eu(NTA-SBA-15)$_3$bpy recorded along the [100] (*top*) and [110] (*bottom*) zone axes (*Right*) (Reprinted with permission from Ref. [51]. Copyright 2008 the American Chemical Society

phen, and RE(Calix-NH$_2$-S15)phen) using modified macrocycle organic ligands (Calix-Si, Calix-NO$_2$-Si, and Calix-NH$_2$-Si) as a linker [58]. Li et al. also functionalize SBA-15 mesoporous silica with two kinds of macrocyclic porphyrin derivatives (meso-(tetra(p-hydroxyphenyl)porphyrin (THPP), protoporphyrin IX (PPIX)) through condensation approach of TEOS [59]. They exhibit the characteristic NIR luminescence of Nd^{3+} and Yb^{3+}.

Li et al. synthesize two kinds of binary and ternary rare earth (Nd^{3+} or Yb^{3+}) hybrid materials using 9-hydroxyphenalen-1-one (HPNP)-modified silane as bridge molecule and phen as assistant ligand, which display the characteristic NIR luminescence of Nd^{3+} and Yb^{3+} under the excitation at visible region [60]. Furtherly, Gu et al. modify MHPO (2-methyl-9-hydroxyphenalenoe) with TESPIC to achieve linkage (MHPOSi) and prepare photoconversion RE^{3+} (Eu^{3+}, Nd^{3+}, Yb^{3+}) mesoporous hybrid materials [61]. The functionalized mesoporous SBA-15 network still presents excitation capability in visible region in spite of the modification of organic silane. Subsequently, they can exhibit characteristic visible (for Eu^{3+}) and NIR

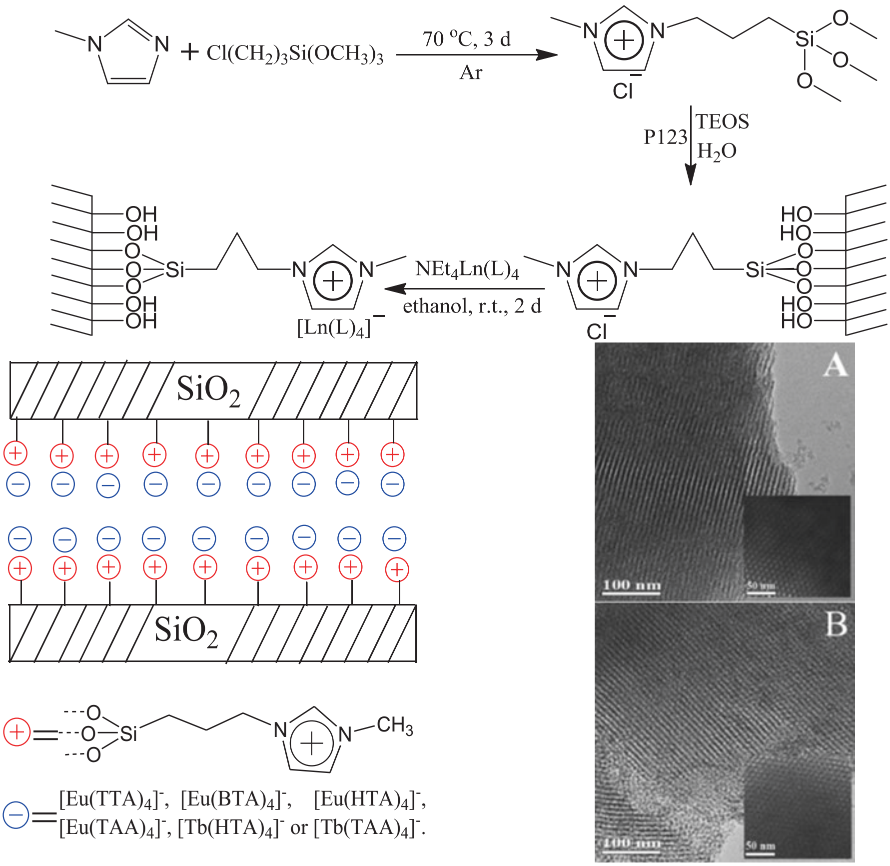

Fig. 3.4 The scheme for the synthesis process and possible structure of the resulted materials (*Top* and *Bottom*, *left*); TEM images of SBA-15-IM$^+$Cl$^-$ (*A*) and SBA-15-IM$^+$[Eu(TTA)$_4$]$^-$ (*B*) (*Bottom, right*) (Reprinted with permission from Ref. [63]. Copyright 2012 the Royal Society of Chemistry)

luminescence for (Nd^+ and Yb^{3+}). The photo conversion between the visible and NIR light can be expected to have potential application in the practical fields. Moreover, Gu et al. synthesize a series of new visible and near-infrared (NIR) luminescent rare earth complexes of hydroxybenz[de]anthracen derivatives ($RE(HBAN)_3(H_2O)_2(NO_3)_3$, $RE(HBAN)_3phen(NO_3)_3$) (HBAN-6-hydroxybenz[de]anthracen-7-one, RE = Eu, Yb, Nd) and prepare the chemically bonded rare earth hybrids of functionalized mesoporous silica (SBA-15) using HBAN-functionalized alkoxysilane (HBAN-Si) as linker [62]. Worth noting here is that the excitation spectra of these hybrid materials are extended to visible light region (439–535 nm). Upon ligand-mediated excitation with the ultraviolet and visible light, the visible luminescence for europium hybrids and NIR luminescence for Yb^{3+} and Nd^{3+} hybrids are obtained.

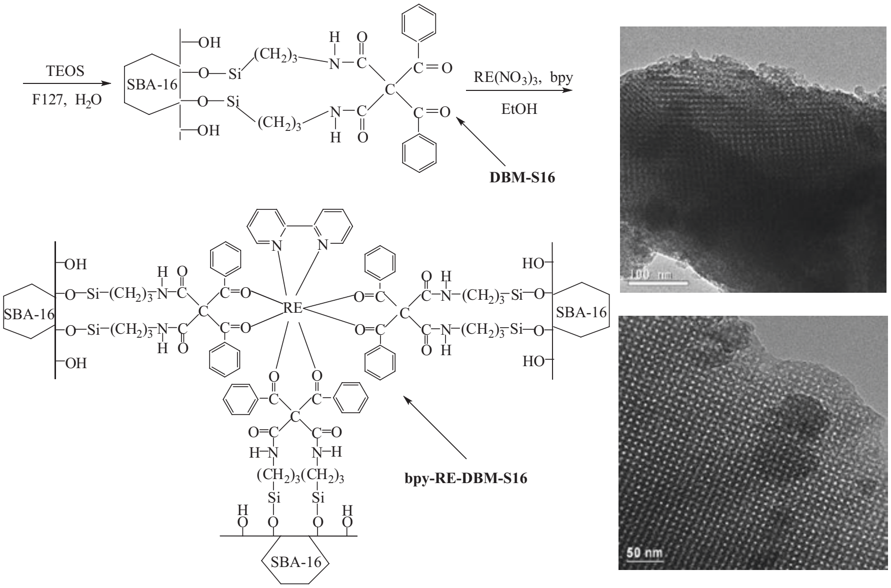

Fig. 3.5 Scheme for synthesis process and predicted structure of mesoporous hybrid materials bpy-RE-TTA-S16 (RE = Eu, Tb) (Left); TEM images of pure SBA-16 (Top) and mesoporous hybrid bpy-Eu-TTA-S16 (Bottom) (Right). Reprinted with permission from [64]. Copyright 2010 Elsevier

Li et al. put forward a novel method to construct the luminescent mesoporous materials, in which the ionic liquid 1-methyl-3-[3-(trimethoxysilyl)propyl] imidazolium chloride is incorporated into mesoporous SBA-15 framework by an in situ sol–gel processing (Fig. 3.4) [63]. Then, an anion metathesis processing is performed for introducing the rare earth β-diketonate complexes anion. Four kinds of commercially available β-diketonate are used in here, which are benzoyltrifluoroacetone (BTA), hexafluoroacetylacetone (HTA), TTA, and trifluoroacetylacetone (TAA), respectively. Subsequently, four europium-based mesoporous materials SBA-15-IM$^+$[Eu(L)$_4$]$^-$ (L = TTA, BTA, HTA, or TAA) are obtained after anchoring the europium β-diketonate complexes anion onto the SBA-15 framework. All the resulting materials through ionic exchange possess higher quantum yields than those covalently bonded mesoporous hybrid materials. This may be due to the fact that ion exchange reaction forming the hybrid system through static force is beneficial for the energy transfer and sensitized luminescence of rare earth ions.

Yan's group prepare mesoporous SBA-16-type hybrids, TTA-S16, and DBM-S16, by co-condensation of a modified β-diketone in the presence of Pluronic F127. Novel mesoporous luminescent hybrids containing RE^{3+} (Eu^{3+}, Tb^{3+}) complexes covalently attached to the functionalized ordered mesoporous SBA-16 (TTA-S16 and DBM-S16), denoted by bpy-Ln-TTA-S16 and bpy-RE-DBM-S16, are obtained by a sol–gel process (Fig. 3.5). The luminescence properties of these resulting materials have been characterized in detail, and the results reveal that the mesoporous hybrid material bpy-Eu-TTA-S16 has a stronger luminescence intensity, longer lifetime, and higher luminescence quantum efficiency than the corresponding DBM-containing material bpy-Eu-DBM-S16, and bpy-Tb-DBM-S16 exhibits a stronger characteristic emission of Tb^{3+} and a longer lifetime than the corresponding TTA-containing material bpy-Tb-TTA-S16 [64]. Further, Gu et al. synthesize rare earth complex functionalized mesoporous SBA-16-type hybrid materials by co-condensation of modified 2-methyl-9-hydroxyphenalenoe (MHPOSi, from the modification of TESPIC and TEOS) [65]. Among them, Eu^{3+} hybrid system shows the ultraviolet excitation and visible emission, and Nd^{+} and Yb^{3+} hybrids exhibit the visible excitation and NIR emission.

3.4 Photofunctional Rare Earth Hybrid Materials Based on POMs-Type Mesoporous Silica

PMOs (periodic mesoporous organosilicas) belong to hybrid materials with organic functional groups that functionalized mesoporous silica host, in which organic groups are contained within the mesoporous pore walls. The organic functional groups are distributed in the mesoporous frameworks and cannot block the channel or occupy the pore volume, whose flexibility can enhance the mechanical strength of materials. Besides, the different organic groups can tune the hydrophilicity/hydrophobicity of the materials surface and also can derive the new active center through further reactions. PMOs realize the uniform distribution and high loading amount of organic groups [15–17].

For mesoporous hybrids with PMO hosts, Guo et al. report novel periodic mesoporous organosilica covalently grafted with phen-derived ORMOSILs (phen-PMO), which is synthesized via co-condensation of 1,2-bis(triethoxysilyl)ethane and phen-Si using a polyoxyethylene stearyl ether surfactant as a template (under acidic conditions) [66]. Compared with the pure complex, the resulting hybrid material exhibits better thermal stability and a similar emission quantum efficiency. Besides, the PMO material is further synthesized through one-step co-condensation of 1,2-bis(triethoxysilyl)ethane (BTESE) and benzoic acid-functionalized organosilane (BA-Si) using cetyltrimethylammonium bromide (CTAB) as a structure-directing agent under basic conditions (Fig. 3.6, Bottom) [67]. XRD and N_2 adsorption–desorption isotherms reveal the characteristic mesoporous structure with highly uniform pore size distributions. FESEM confirms that the morphology of the PMOs is significantly dependent on the molar ratio of two organosilica precursors. In addition, BA-PMO is attempted as a supporter to link the Tb^{3+} ions via impregnation of $TbCl_3$ into BA-PMO through a ligand exchange reaction. Under the UV radiation, it exhibits a strong characteristic of emitting Tb^{3+} ions.

More recently, Sun et al. prepare periodic mesoporous organosilica material (named as bpd-PMO) through co-condensation of bis(triethoxysilyl)ethane (BTEE)

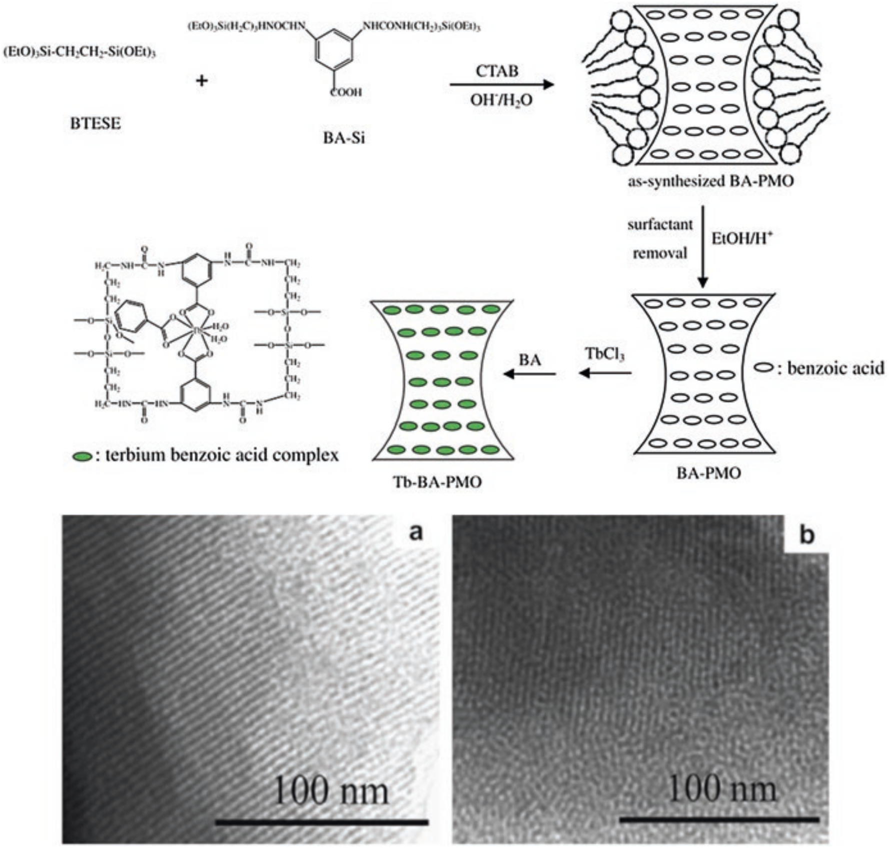

Fig. 3.6 (*Top*) Schematic diagram for synthesis of the novel PMO via a co-condensation of 1,2-bis(triethoxysilyl)ethane (BTESE) and benzoic acid-functionalized organosilane (BA-Si) and its application in incorporation of the Tb^{3+} ions as matrix. (*Bottom*) TEM images of hybrid Tb-BA(0.07)-PMO material recorded along the [100] (*a*) and [110] (*b*) zone axes (Reprinted with permission from Ref. [67]. Copyright 2009 Elsevier)

and a synthesized silsesquioxane precursor 4,4′-bis[$Si(OEt)_3(CH_2)_4$]-2,2′-bipyridine (bpd-Si) [68]. Subsequently, three NIR-luminescent PMO hybrid materials (named as $RE(DBM)_3$bpd-PMO, RE = Er, Nd, Yb) covalently linked with rare earth complexes are prepared via a ligand exchange reaction. The excitation spectra of the $RE(DBM)_3$bpd-PMO extend to the visible light range, whose visible light excitation produces the characteristic NIR luminescence of the corresponding RE^{3+} ions.

In recent years, Li et al. synthesize PMOs by linking rare earth (Tb^{3+}, Eu^{3+}) complexes to mesoporous frameworks through modified 4-mercaptobenzoic acid (MCBA) [69]. From the 29Si MAS NMR spectra, the peaks corresponding to the organosiloxane T_n [$T_n = RSi(OSi)_nOH_{3-n}$, n = 2–3] species can be identified clearly, which indicates the existence of the Si–C bond in the hybrids. Besides, the relative intensity of T_3 NMR signal is obviously stronger than T_2, resulting in the degree of

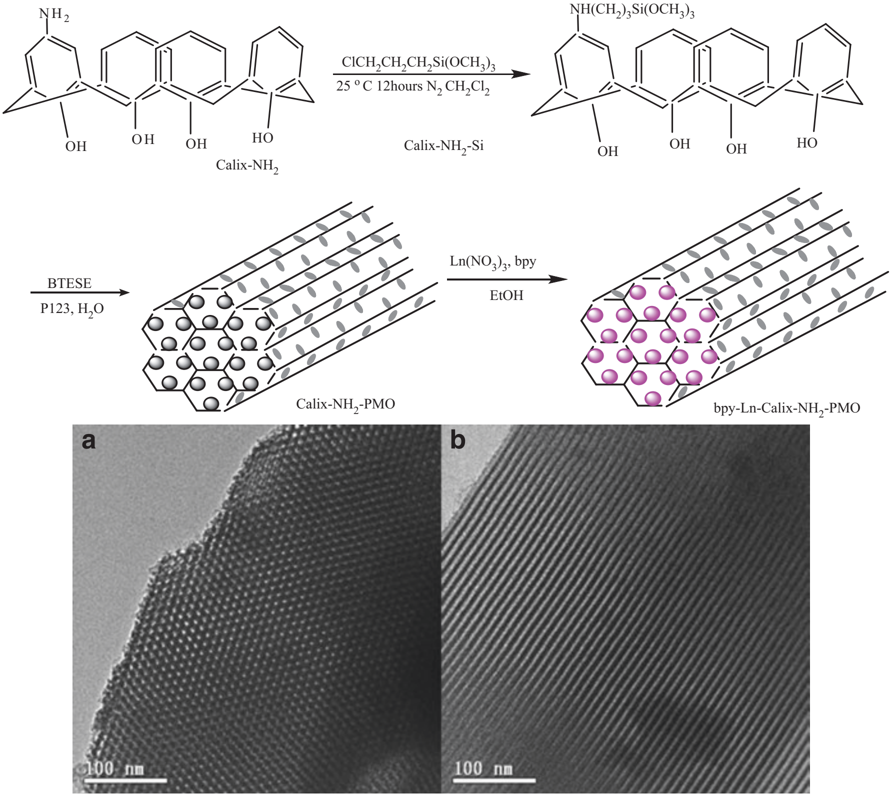

Fig. 3.7 Scheme for synthesis (*Top*) and high-resolution transmission electron microscopy images (*Bottom*) of ternary mesoporous hybrid bpy-Tb-Calix-NH_2-PMO recorded along the [100] (*A*) and [110] (*B*) zone axes (Reprinted with permission from Ref. [70]. Copyright 2011 the Royal Society of Chemistry Publishing Company)

hydrolysis–condensation between BTESE and MCBA is completely. The absence of various siloxane Q_m [$Q_m = Si(OSi)_m (OH)_{4-m}$, m = 2–4] around −90 to −120 ppm suggests that Si–C bond is not decomposed in the process of hydrolysis–condensation. Recently, Li et al. prepare the ternary mesoporous hybrid material bpy-Ln-Calix-NH_2-PMO (Ln = Eu, Tb) by linking ternary rare earth (Eu^{3+}, Tb^{3+}) complexes to PMOs through functionalized Calix-NH_2 ligands [70]. The luminescence properties show that the triple-state energy level of Calix-NH_2 is more suitable for the sensitization of Eu^{3+} than of Tb^{3+}, and the luminescence intensity of the $^5D_0 \rightarrow {}^7F_2$ transition and the $^5D_0$ luminescence quantum efficiency of this material are higher than that of the pure bpy-Eu-Calix-NH_2 complex, further confirming that the ternary complex bpy-Ln-Calix-NH_2 is covalently bonded to the PMO silicon network (see Fig. 3.7).

Gu et al. use molecular linkage phen-Si to construct the phen-NH_2-functionalized periodic mesoporous organosilica (PMOs) hybrids by linking ternary europium complexes with phen-Si linkage and MHPO [71]. It is worth pointing out that the europium hybrids show emission of both europium ion and phen-functionalized PMOs, which can be integrated into the close white luminescence. This provides us a strategy to obtain white emissive rare earth hybrids.

3.5 Photofunctional Rare Earth Hybrid Materials Based on Organically Modified Mesoporous Silica and Other Inorganic Hosts

From above introduction to the three main kinds of organically modified mesoporous silica hybrid materials, we can draw a conclusion that the covalent linker still plays an important role in preparing these mesoporous hybrids by postsynthetic modification and in situ assembly approach. Besides, some work report the comparison of different mesoporous hosts except for the assembly process using different templates. For example, Sun et al. achieve the NIR-luminescent RE(DBM)$_3$phen complexes covalently bonded to the ordered mesoporous materials MCM-41 and SBA-15 via a functionalized phen group phen-Si (RE = Er, Nd, Yb) [72]. The synthesis parameters $X = 12$ and $Y = 6$ h (X denotes RE(DBM)$_3$(H$_2$O)$_2$/phen-MCM-41 molar ratio or RE(DBM)$_3$(H$_2$O)$_2$/phen-SBA-15 molar ratio and Y is the reaction time for the ligand exchange reaction) are selected through a systematic and comparative study. The derivative materials are denoted as RE(DBM)$_3$phen-MCM-41 and RE(DBM)$_3$phen-SBA-15 (RE = Er, Nd, Yb). In addition, RE(DBM)$_3$phen-SBA-15 hybrids show an overall increase in relative luminescent intensity and lifetime compared to the RE(DBM)$_3$phen-MCM-41 materials, which is explained by the comparison of the rare earth ion content and the pore structures of the two kinds of mesoporous materials. Li et al. also prepare rare earth mesoporous hybrid l materials by introducing the ternary rare earth (Eu^{3+}, Tb^{3+}) β-diketonate (TTA, TAA) into the functionalized mesoporous hosts through the coordination bond and covalent bond by using 3-chloropropyltriethoxysilane modified 1,4,7, 10-tetraazacyclododecane (Cyclen-Si) as an organic bridge molecule [73]. Gu et al. prepare a series of hybrid materials by linking rare earth (Eu^{3+}, Sm^{3+}) complexes to mesoporous SBA-15/SBA-16 through 8-hydroxybenz[de]anthracen-7-one modified silane (HBA-Si) as linker [74]. The luminescence properties of these covalently bonded materials (denoted as RE(HBA-SBA-15)$_3$phen and RE(HBA-SBA-16)$_3$phen) are compared with ternary complexes (RE(HBA)$_3$phen) (RE = Eu, Sm). Eu(HBA-SBA-15(16))$_3$phen hybrids display better thermal stability; their luminescent lifetimes and quantum efficiencies are comparable to those of Eu(HBA)$_3$phen complex in spite of its much less effective condensation of Eu^{3+} species. In addition, the luminescent performance of functionalized SBA-15 hybrids is more favorable than that of functionalized SBA-16 hybrids, revealing that SBA-15 is a better host material for rare earth complex than mesoporous silica SBA-16. Guo et al. prepare ternary Eu(TTA)$_3$phen covalently bonded with the general mesoporous material

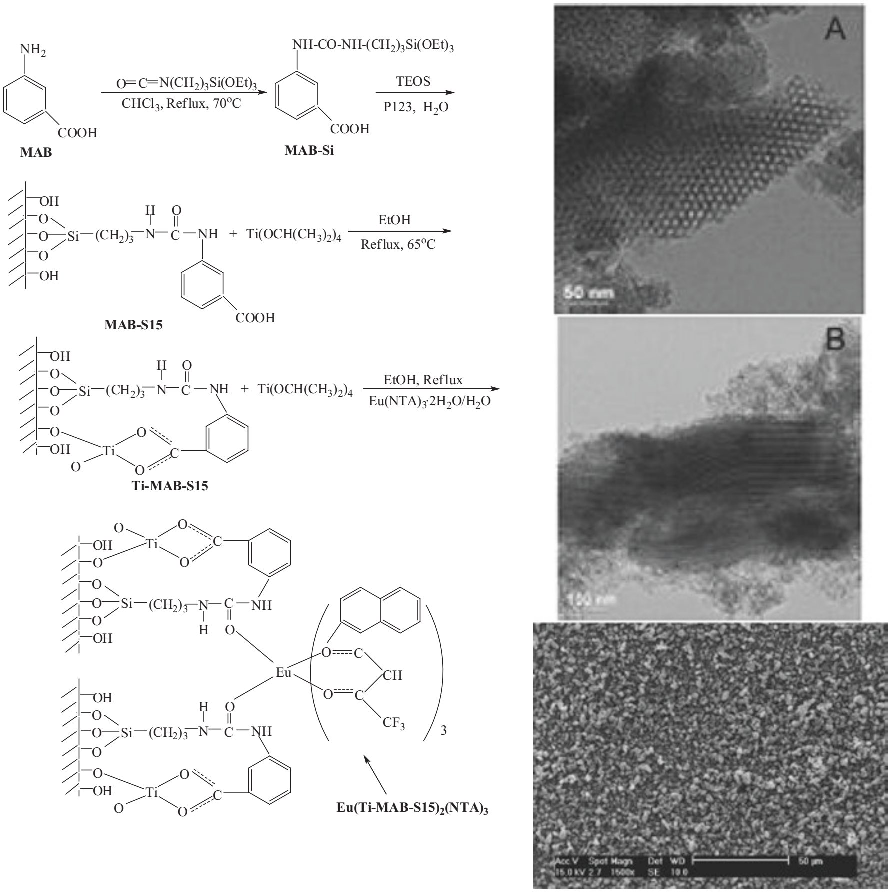

Fig. 3.8 The scheme for synthesis procedure and predicted structure of the (*Left*), TEM images (*top, middle*) recorded along the [100] (*A*) and [110] (*B*) zone axes and SEM image (*bottom*) of mesoporous ternary hybrid titania materials Eu(Ti-MAB-S15)$_2$(NTA)$_3$ (*Right*) (Reprinted with permission from Ref. [76]. Copyright 2011 the Royal Society of Chemistry Publishing Company)

SBA-15 and SBA-15-type of periodic mesoporous organosilica (PMO) material via impregnation of Eu(TTA)$_3$·2H$_2$O into phen-S15 and phen-PMO, respectively, through a ligand exchange reaction [75]. Compared with the sample of Eu(TTA)$_3$phen-PMO, the mesoporous hybrid material Eu(TTA)$_3$phen-S15 exhibits longer luminescent decay time and higher luminescence intensity, emission quantum efficiency, and absolute quantum yield. Meanwhile, the result of thermal treatment demonstrates that the europium complex in Eu(TTA)$_3$phen-S15 material possesses a better thermal stability than that in Eu(TTA)$_3$phen-PMO.

Li et al. prepare multifunctional precursor Ti-MAB-S15 (MAB = meta-aminobenzoic acid) through the reaction of the carboxylic group with titanium alkoxide, and the amino group is modified with the coupling agent TESPIC and covalently bonded to mesoporous silica SBA-15 (Fig. 3.8) [76]. The selection of ligand is the key point for the preparation of this hybrid material. Herein, the organic ligand MAB is selected as multifunctional linker, which not only can be covalently bonded to the framework of mesoporous silica and coordinate to lanthanide ions as well as sensitize the luminescence of them, but also can modify the reactivity of titanium precursor and introduce titania matrix to the hybrid system. Then, novel luminescent mesoporous hybrid titania materials Eu(Ti-MAB-S15)$_2$(NTA)$_3$ are obtained by introducing the Eu(NTA)$_3$·2H$_2$O complex into the hybrid materials Ti-MAB-S15 via a ligand exchange reaction. Compared to the pure complex Eu(NTA)$_3$·2H$_2$O, the mesoporous hybrid titania material Eu(Ti-MAB-S15)$_2$(NTA)$_3$ presents longer luminescent lifetime and higher quantum efficiency, which indicates that the introduction of the multifunctional ligand Ti-MAB-S15 can sensitize the luminescence emission of Eu^{3+} ions.

In addition, they further put forward a novel method to assemble luminescent rare earth hybrid materials containing ordered mesoporous Si–O network and amorphous Ti–O (Al–O) network simultaneously (Fig. 3.9) [77]. Firstly, NTA-functionalized SBA-15 mesoporous hybrid material (NTA-S15) is prepared, in which NTA is covalently bonded to the framework SBA-15 by co-condensation of modified NTA (denoted as NTA–Si) and TEOS. Subsequently, nicotinic acid (NA) is selected as the second ligand, whose carboxylic acid group can react with metallic alkoxide to moderate the reactivity toward hydrolysis and condensation, and the heterocyclic group can coordinate to rare earth ions as well as sensitize the luminescence of them. Finally, after the coordination reaction between rare earth ions and functionalized organic ligand (NTA-S15 and NA-M (M = Ti, Al)) together with the hydrolysis cross-linking reaction, the final mesoporous hybrids Ln(NA-M)$_2$(NTA-S15)$_3$ (Ln = Eu, Tb; and M = Ti, Al) are obtained. Further investigation on the luminescence properties shows that the lanthanide mesoporous material containing Al–O network presents stronger luminescence intensities, longer lifetimes, and higher luminescence quantum efficiencies than the lanthanide mesoporous hybrids containing Ti–O network, which indicates Al–O network is a better candidate host for supporting the lanthanide complex than Ti–O network.

Pang et al. recently prepare the luminescent mesoporous hybrids, Eu(M-BDA)$_2$(TTA-SBA-15)$_3$ and Eu(M-BDA)$_2$(TTA-MCM41)$_3$ (M = Ti, Al) through the coordination reaction between Eu^{3+} ions and a functionalized organic ligand (TTA-SBA-15 or TTA-MCM41 and M-BDA (M = Ti, Al)) followed by the hydrolysis cross-linking reaction [78]. Results show that SBA-15-type mesoporous hybrid Eu(M-BDA)$_2$(TTA-SBA-15)$_3$, with larger pore sizes than the corresponding MCM-41-type hybrids Eu(M-BDA)$_2$(TTA-SBA-15)$_3$, presents longer luminescent lifetimes and higher quantum efficiency than the latter because of spatial confinements of mesoporous matrix nanochannels. The Al–O-based mesoporous hybrids also exhibit more excellent luminescent properties than the corresponding Ti–O-based hybrids, suggesting that the Al–O host is more beneficial to Eu^{3+} ion luminescence than the Ti–O host. The quantum efficiency of Eu(Al-BDA)(TTA-SBA-15)$_3$ is high, even up to 43%.

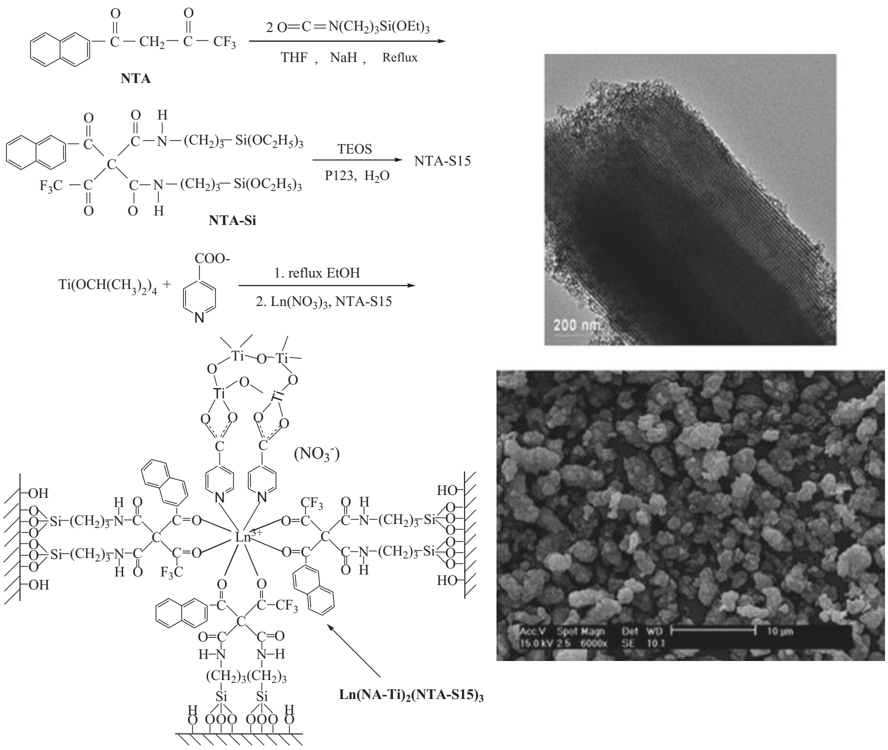

Fig. 3.9 The scheme for synthesis procedure and predicted structure (*Left*), TEM and SEM images (*Right*) of mesoporous hybrid materials RE(NA-Ti)$_2$(NTA-S15)$_3$ (RE = Eu, Tb) (Reprinted with permission from Ref. [77]. Copyright 2011 the Royal Society of Chemistry Publishing Company)

3.6 Photofunctional Rare Earth Hybrid Materials Based on Organically Modified Mesoporous Silica and Polymer Units

Fu et al. incorporate diurea cross-linked poly(oxyethylene) (POE)/siloxane hybrid structure (di-ureasil) into the hexagonal array of one-dimensional channels of mesoporous silica MCM-41 [79]. The hybrids display the intrinsic green emission of MCM-41 superposed to the blue and purplish-blue di-ureasil components. Time-resolved spectroscopy provides further support from energy transfer between the mesoporous silica and the di-ureasil matrix.

Yan’s group focus on the research of ternary assembly of organically modified mesoporous silica and polymer unit by means of the postsynthetic technology [80–83]. Li et al. first assemble the mesoporous luminescent polymeric hybrid materials containing rare earth (Eu^{3+}, Tb^{3+}) complexes covalently bonded to mesoporous silica SBA-15 [81]. The detailed luminescence studies on all the materials show that the ternary rare earth mesoporous polymeric hybrid materials present stronger luminescent intensities, longer lifetimes, and higher luminescent quantum efficiencies than the binary rare earth mesoporous hybrid materials, indicating that the introduction of the organic polymer chain is beneficial for the luminescence properties of the overall hybrid system. Further, they conduct the systematic and comparative study of the mesoporous materials covalently bonded with rare earth complexes containing organic polymeric chains, designated as Ln(DBM-SBA-15)$_3$PMAA and Ln(DBM-SBA-16)$_3$PMAA (Ln = Eu, Tb; DBM-SBA-15 and DBM-SBA-16 denote DBM-functionalized SBA-15 mesoporous material and DBM-functionalized SBA-16 material, respectively) (Fig. 3.10) [81]. In addition, for further comparison, SBA-15 and SBA-16 covalently bonded with the binary Ln^{3+} complex with DBM ligand are also synthesized, denoted as Ln(DBM-SBA-15)$_3$ and Ln(DBM-SBA-16)$_3$ (Ln = Eu, Tb), respectively. The luminescence properties of all synthesized materials are comprehensively characterized and compared.

Li et al. further compare a series of ternary mesoporous polymeric hybrids, TTA-S16-Eu-PMMA, TTA-S16-Eu-PMAA, and TTA-S16-Eu-PVP (PVP = polyvinylpyrrolidone), which are assembled by the Eu^{3+} complex covalently attached to the TTA directly functionalized ordered mesoporous SBA-16 and three organic polymers [82]. The ternary rare earth mesoporous polymeric hybrids show an overall increase in luminescent lifetime and quantum efficiency compared to binary rare earth mesoporous hybrid TTFA-S16-Eu, especially the mesoporous hybrid with PVP exhibits the highest luminescence quantum efficiency and longest lifetime. Gu et al. prepare polymeric mesoporous hybrid materials containing europium (III) complexes incorporated to mesoporous silica SBA-15/SBA-16 by simple physical doping (impregnation) methods, followed by the additional polymerization reaction of the monomer 4-vinylpyridine (vpd) extending along the mesoporous channels [83]. After the physical doping and the polymerization reaction, the final ternary materials Eu(β-diketonate)$_3$pvpd-SBA-15/Eu(β-diketonate)$_3$pvpd-SBA-16 are obtained. The XRD and BET results reveal that all of these hybrid materials have uniformity in the mesostructure. The detailed luminescence investigation on all the materials shows that Eu(TAA)$_3$pvpd-SBA-16 has the highest luminescence intensity and the materials with TAA ligands have longer lifetimes.

Li et al. realize the linkage of the binary and ternary Eu^{3+} complexes to the functionalized ordered mesoporous SBA-15 with the modified polymer poly(ethylene glycol) (PEG) as a “bifunctional bridge,” where PEG is firstly modified with the coupling agent TESPIC and covalently bonded to mesoporous silica SBA-15 (designated as PEG-SBA-15) [84]. They further prepare polymer-functionalized mesoporous SBA-16-type hybrid materials with encapsulated rare earth (Eu^{3+} and Tb^{3+}) complexes for luminescence. The organic molecule acrylamide (AM) is modified by a silane coupling agent TESPIC to form an alkene precursor, which is then covalently bonded to a mesoporous SBA-16 backbone [85]. Then, the flexible polymer chain polyacrylamide (PAM) within the pores of SBA-16 can be formed by initiating the monomer. The luminescent mesoporous hybrids (denoted as RE(S16-PAM-Si)$_3$ and RE(S16-PAM-Si)$_3$phen, respectively) with the organic polymer acting as a flexible linker between the mesoporous framework and the rare earth complex are finally attained.

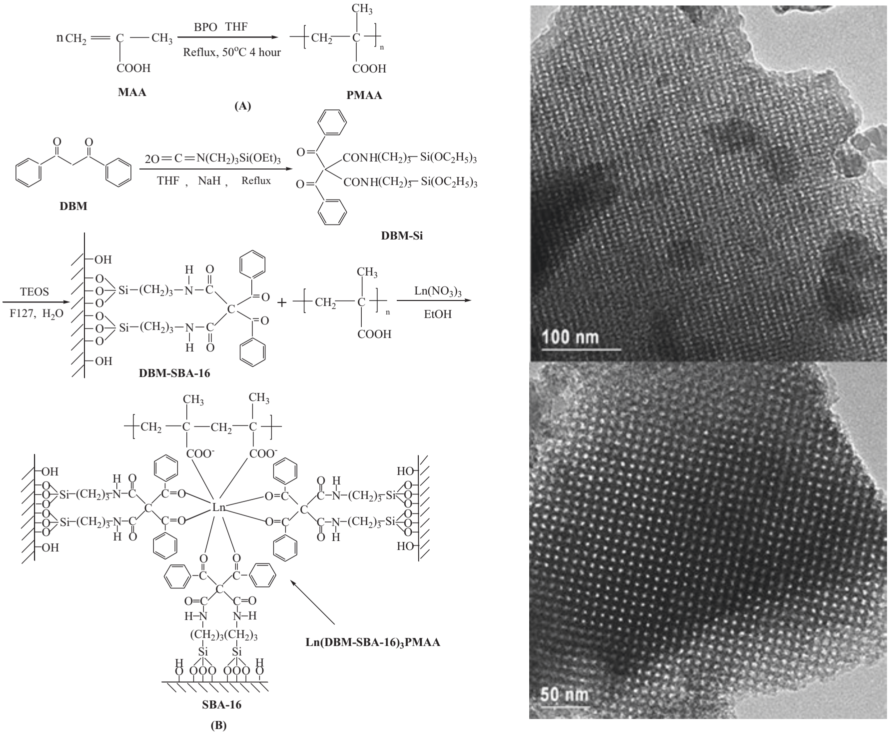

Fig. 3.10 Selected scheme of synthesis process of PMAA (*A*) and the mesoporous polymeric hybrids Ln(DBM-SBA-16)$_3$PMAA (*B*) (*Left*); HRTEM images of Eu(DBM-SBA-15)$_3$PMAA (*top*) and Eu(DBM-SBA-16)$_3$PMAA (*bottom*) (*Right*) (Reprinted with permission from Ref. [81]. Copyright 2010 the Royal Society of Chemistry)

3.7 Conclusion and Outlook

In conclusion, recent research progress in the photofunctional rare earth hybrid materials based on mesoporous silica has been summarized, which mainly consist of three important classes with the different mesoporous hosts to be functionalized. The first is the rare earth hybrids based on MCM-41(or 48). The second is the rare earth hybrids based on SBA-51(or 16). The third is the rare earth hybrids based on POMs. Among all the results, it is suggested that SBA-15 is the most favorable host for the luminescence of rare earth ions, whose mesoporous hybrids display the best luminescent performance. Besides, both inorganic host and organic polymer host can be introduced to the mesoporous hybrid materials, providing new opportunities to obtain new systems and new applications. However, some problems still exist in the field of photofunctional rare earth materials based on mesoporous silica. The most important one is how to develop the practical applications of these materials.

References

1. Lebeau B, Galarneau A, Linden M (2013) Introduction for 20 years of research on ordered mesoporous materials. Chem Soc Rev 42:3661–3662
2. Kresge CT, Roth WJ (2013) The discovery of mesoporous molecular sieves from the twenty year perspective. Chem Soc Rev 42:3663–3670
3. Chong ASM, Chong ZXS (2003) Functionalization of SBA-15 with APTES and characterization of functionalized materials. J Phys Chem B 107:12650–12657
4. Sayari A, Yang Y, Kruk M, Jaroniec M (1999) Expanding the pore size of MCM-41 silicas: use of amines as expanders in direct synthesis and postsynthesis procedures. J Phys Chem B 103:3651–3658
5. Mehdi A, Reye C, Corriu R (2011) From molecular chemistry to hybrid nanomaterials. Design and functionalization. Chem Soc Rev 40:563–574
6. Mizoshita N, Tani T, Inagaki S (2011) Syntheses, properties and applications of periodic mesoporous organosilicas prepared from bridged organosilane precursors. Chem Soc Rev 40:789–800
7. Kresge CT, Leonowicz ME, Roth WJ, Vartuli JC, Beck JS (1992) Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism. Nature 359:710–712
8. Beck JS, Vartuli JC, Roth WJ, Leonowicz ME, Kresge CT, Schmitt KD, Chu CT, Olson DH, Sheppard EW, McCullen SB, Higgins JB, Schlenker JL (1992) A new family of mesoporous molecular sieves prepared with liquid crystal templates. J Am Chem Soc 114:10834–10843
9. Scott J, Wirnsberger G, Stucky GD (2001) Mesoporous and mesostructured materials for optical applications. Chem Mater 13:3140–3150
10. Lim MH, Stein A (1999) Comparative studies of grafting and direct synthesis of inorganic-organic hybrid mesoporous materials. Chem Mater 11:3285–3295
11. Zhao DY, Feng JP, Huo QS, Melosh N, Fredrickson CH, Chmelka BF, Stucky GD (1998) Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores. Science 279:548–552
12. Zhao DY, Sun JY, Li QZ, Stucky GD (2000) Morphological control of highly ordered mesoporous silica SBA-15. Chem Mater 12:275–278
13. Newalkar BL, Komarneni S, Katsuki H (2000) Rapid synthesis of mesoporous SBA-15 molecular sieve by a microwave– hydrothermal process. Chem Comm:2389–2390
14. Zhao DY, Huo QS, Feng JP, Chmelka BF, Stucky GD (1998) Nonionic triblock and star diblock copolymer and oligomeric surfactant syntheses of highly ordered, hydrothermally stable, mesoporous silica structures. J Am Chem Soc 120:6024–6036
15. Melde BJ, Holland BT, Blanford CF, Stein A (1999) Mesoporous sieves with unified hybrid inorganic/organic frameworks. Chem Mater 11:3302–3308
16. Inagaki S, Guan S, Fukushima Y, Ohsuna T, Terasaki O (1999) Novel mesoporous materials with a uniform distribution of organic groups and inorganic oxide in their frameworks. J Am Chem Soc 121:9611–9614
17. Asefa T, MacLachlan MJ, Coombs N, Ozin GA (1999) Periodic mesoporous organosilicas with organic groups inside the channel walls. Nature 402:867–871
18. Smith JV (1988) Topochemistry of zeolites and related materials. I. Topology and geometry. Chem Rev 88:149–182
19. Mann S (1993) Molecular tectonics in biomineralization and biomimetic materials chemistry. Nature 365:499–505
20. Shephard DS, Zhou WS, Maschmeyer T (1998) Site directed surface derivatization of electron microscopy MCM-41: use of high-resolution transmission and molecular recognition for determining the position of functionality within mesoporous materials. Angew Chem Int Edi 37:2719–2723
21. Burket SL, Sims SD, Mann S (1996) Synthesis of hybrid inorganic–organic mesoporous silica by co-condensation of siloxane and organosiloxane precursors. Chem Comm:1367–1368

22. Fowler CE, Burkett SL, Mann S (1997) Synthesis and characterization of ordered organo–silica–surfactant mesophases with functionalized MCM-41-type architecture. Chem Comm:1769–1770
23. Stein A, Melde BJ, Schroden RC (2000) Hybrid inorganic-organic mesoporous silicates - nanoscopic reactors coming of age. Adv Mater 12:1403–1419
24. Xu QH, Li LS, Li B, Yu JH, Xu RR (2000) Encapsulation and luminescent property of tetrakis(1-(2-thenoyl)-3,3,3-triuoracetate) europium N-hexadecyl pyridinium in modi®ed Si±MCM-41. Microp Mesop Mater 38:351–358
25. Fu LS, Xu QH, Zhang HJ, Li LS, Meng QG, Xu RR (2002) Preparation and luminescence properties of the mesoporous MCM-41s intercalated with rare earth complex. Mater Sci Eng B 88:68–72
26. Xu QH, Li LS, Liu XS, Xu RR (2002) Incorporation of rare-earth complex $Eu(TTA)_4C_5H_5NC_{16}H_{33}$ into surface-modified Si-MCM-41 and its photophysical properties. Chem Mater 14:549–555
27. Xu QH, Dong WJ, Li HW, Li LS, Feng SH, Xu RR (2003) Encapsulation and luminescent property of $[C_5H_5NC_{16}H_{33}][Eu(TTA)_4]$ (TTA: tetrakis(1-(2-thenoy)-3,3,3-trifluoracetate) in chiral Si-MCM-41. Solid State Sci 5:777–782
28. Gago S, Fernandes JA, Rainho JP, Ferreira RAS, Pillinger M, Valente AA, Santos TM, Carlos LD, Ribeiro-Claro PJA, Goncalves IS (2005) Highly luminescent tris(β-diketonate) europium(III) complexes immobilized in a functionalized mesoporous silica. Chem Mater 17:5077–5084
29. Bruno SM, Coelho AC, Ferreira RAS, Carlos LD, Pillinger M, Valente AA, Ribeiro-Claro P, Gonçalves IS (2008) MCM-41 derivatised with pyridyl groups and its use as a support for luminescent europium(III) complexes. Eur J Inorg Chem 2008:3786–3795
30. Bruno SM, Ferreira RAS, Carlos LD, Pillinger M, Ribeiro-Claro P, Gonçalves IS (2008) Synthesis, characterization and luminescence properties of MCM-41 impregnated with an Eu^{3+} β-diketonate complex. Microp Mesop Mater 113:453–462
31. Felício MR, Nunes TG, Vaz PM, Botas AMP, Ribeiro-Claro P, Ferreira RAS, Freire RO, Vaz PD, Carlos LD, Nunes CD, Nolasco MM (2014) Modelling the luminescence of extended solids: an example of a highly luminescent MCM-41 impregnated with a Eu^{3+} β-diketonate complex. J Mater Chem C 2:9701–9711
32. Li HR, Lin J, Fu LS, Guo JF, Meng QG, Liu FY, Zhang HJ (2002) Phenanthroline-functionalized MCM-41 doped with europium ions. Microp Mesop Mater 55:103–107
33. Sun LN, Yu JB, Zhang HJ, Meng QG, Ma E, Peng CY, Yang KY (2007) Near-infrared luminescent mesoporous materials covalently bonded with ternary rare earth [Er(III), Nd(III), Yb(III), Sm(III), Pr(III)] complexes. Microp Mesop Mater 98:156–165
34. Sun LN, Zhang Y, Yu JB, Yu SY, Dang S, Peng CY, Zhang HJ (2008) Design and synthesis of near-IR luminescent mesoporous materials covalently linked with tris(8-hydroxyquinolinate) rare earth(III) complexes. Microp Mesop Mater 115:535–540
35. Feng J, Song SY, Xing Y, Zhang HJ, Li ZF, Sun LN, Guo XM, Fan WQ (2009) Synthesis, characterization, and near-infrared luminescent properties of the ternary thulium complex covalently bonded to mesoporous MCM-41. J Solid State Chem 182:435–441
36. Feng J, Song SY, Fan WQ, Sun LN, Guo XM, Peng CY, Yu JB, Yu YN, Zhang HJ (2009) Near-infrared luminescent mesoporous MCM-41 materials covalently bonded with ternary thulium complexes. Microp Mesop Mater 117:278–284
37. Li Y, Yan B (2008) Hybrid materials of MCM-41 functionalized by rare earth (Tb^{3+}, Eu^{3+}) complexes of modified *meta*-methylbenzoic acid: covalently bonded assembly and photoluminescence. J Solid State Chem 181:1032–1039
38. Li Y, Yan B (2009) Photophysical properties of rare earth hybrids covalently bonded to functionalized MCM-41 by modified aromatic carboxylic acids. J Fluorescence 19:191–201
39. Li Y, Yan B (2010) Rare earth (Tb^{3+}, Eu^{3+}) functionalized MCM-41 through modified *meta*-aminobenzoic acid linkage: covalently bonding assembly, physical characterization and photoluminescence. Microp Mesop Mater 128:62–70

40. Yan B, Zhou B (2008) Two photoactive rare earth (Eu^{3+}, Tb^{3+}) hybrid materials of modified beta-diketone bridge directly covalently bonded mesoporous host (MCM-41). J Photochem Photobiol A Chem 195:314–322
41. Yan B, Li Y, Zhou B (2009) Covalently bonding assembly and photophysical properties of luminescent molecular hybrids Eu-TTA-Si and Eu-TTASi-MCM-41 by modified thenoyltrifluoroacetone. Microp Mesop Mater 120:317–324
42. Li YJ, Yan B, Wang L (2011) Rare earth (Eu^{3+}, Tb^{3+}) Mesoporous hybrids with calix[4]arene derivative covalently linking MCM-41: physical characterization and photoluminescence property. J Solid State Chem 184:2571–2579
43. Gu YJ, Yan B (2013) Europium (III) complex functionalized Si-MCM-41 hybrid materials with visible-light-excited luminescence. Inorg Chim Acta 408:96–102
44. Meng QG, Boutinaud P, Franville AC, Zhang HJ, Mahiou R (2003) Preparation and characterization of luminescent cubic MCM-48 impregnated with an Eu^{3+} β-diketonate complex. Microp Mesop Mater 65:127–136
45. Meng QG, Boutinaud P, Zhang HJ, Mahiou R (2007) Luminescence properties of Eu^{3+} β-diketonates incorporated in cubic mesoporous silica. J Lumin 124:15–22
46. Peng CY, Zhang HJ, Meng QG, Li HR, Yu JB, Guo JF, Sun LN (2005) Synthesis and luminescence properties of SBA-15 functionalized with covalently bonded ternary europium complex. Inorg Chem Comm 8:440–443
47. Peng CY, Zhang HJ, Fu LS, Meng QG, Fu LS, Li HR, Sun LN, Guo XM (2005) Synthesis, characterization, and luminescence properties of the ternary europium complex covalently bonded to mesoporous SBA-15. J Phys Chem B 109:15278–15287
48. Corriu RJP, Mehdi A, Reye C, Thieuleux C, Frenkel A, Gibaud A (2004) Preparation of ordered SBA-15 mesoporous silica containing chelating groups. Study of the complexation of EuIII inside the pore channels of the materials. New J Chem 28:156–160
49. Sun LN, Zhang HJ, Yu JB, Yu SY, Peng CY, Dang S, Guo XM, Feng J (2008) Near-infrared emission from novel tris(8-hydroxyquinolinate)rare earth(III) complexes-functionalized mesoporous SBA-15. Langmuir 24:5500–5507
50. Sun LN, Zhang Y, Yu JB, Peng CY, Zhang HJ (2008) Ternary rare earth (Er^{3+}, Nd^{3+}, Yb^{3+}, Sm^{3+}, Pr^{3+}) complex-functionalized mesoporous SBA-15 materials that emit in the near-infrared range. J Photochem Photobiol A Chem 199:57–63
51. Li Y, Yan B, Yang H (2008) Construction, characterization, and photoluminescence of mesoporous hybrids containing europium (Ш) complexes covalently bonded to SBA-15 directly functionalized by modified *beta*-diketone. J Phys Chem C 112:3959–3968
52. Kong LL, Yan B, Li Y (2009) Hybrid materials of SBA-15 functionalized by Tb^{3+} complexes of modified acetylacetone: covalently bonded assembly and photoluminescence. J Alloys Compds 481:549–554
53. Kong LL, Yan B, Li Y (2009) Mesoporous hybrids containing Eu^{3+} complexes covalently bonded to SBA-15 functionalized: assembly, characterization and photoluminescence. J Solid State Chem 182:1631–1637
54. Yan B, Li Y (2010) Luminescent ternary inorganic-organic mesoporous hybrids Eu(TTASi-SBA-15)phen: covalent linkage in TTA directly functionalized SBA-15. Dalton Trans 39:1480–1487
55. Li YJ, Yan B, Li Y (2010) Luminescent rare earth (Eu^{3+}, Tb^{3+}) ternary mesoporous hybrids with functionalized β-diketones (TTA, DBM) covalently linking SBA-15 and 2,2′-bpyridine (bpy). Microp Mesop Mater 131:82–88
56. Li YJ, Yu XD, Wang XJ, Yang ML (2014) Rare earth (Eu^{3+}, Tb^{3+}) functionalized SBA-15 through modified hexafluoroacetylacetone linkage: covalently bonding construction, physical characterization, and luminescent properties. J Mater Res 29:675–683
57. Li YY, Yan B, Guo L, Li YJ (2012) Ternary rare earth sulfoxide-functionalized mesoporous hybrids Phen-RE(OBDS(BSAB))$_3$-SBA-15 (RE = Eu, Tb): covalently bonded assembly, characterization, and photoluminescence. Microp Mesop Mater 148:73–79

58. Li YJ, Yan B, Wang L (2011) Calix[4]arene derivative functionalized rare earth (Eu, Tb) SBA-15 mesoporous hybrids with covalent bond: assembly, characterization and photoluminescence. Dalton Trans 40:6722–6731
59. Yan B, Li YY, Qiao XF (2012) Photofunctional metalloporphryns functionalized mesoporous hybrids phen-ln(LSi)-SBA-15 (ln = Nd, Yb, L = porphyrin derivatives). Microp Mesop Mater 158:129–136
60. Li YY, Yan B, Qiao XF (2013) Visible light excitation and near-infrared luminescence of rare earth mesoporous hybrids through 9-hydroxyphenalen-1-one linkage by chemical bonds. Microp Mesop. Mater 169:60–66
61. Gu YJ, Yan B (2013) Novel photoversion rare earth functionalized SBA-15 mesoporous hybrids: ultraviolet-visible excitation and visible-NIR emission. Eur J Inorg Chem:2963–2970
62. Gu YJ, Yan B (2013) Rare earth mesoporous SBA-15 hybrids through functionalized 6-hydroxybenz[de]anthracen-7-one linkage: UV-visible light sensitization and visible-NIR luminescence. J Coll Interf Sci 393:36–43
63. Li QP, Yan B (2012) Luminescent hybrid materials of rare earth β-diketonate and mesoporous host through the covalent and ion bonding with anion metathesis. Dalton Trans 41:8567–8574
64. Li YJ, Yan B, Li Y (2010) Hybrid materials of SBA-16 functionalized by rare earth (Eu^{3+}, Tb^{3+}) complexes of modified β-diketone (TTA and DBM): covalently bonding assembly and photophysical properties. J Solid State Chem 183:871–877
65. Gu YJ, Yan B, Qiao XF (2013) Novel light conversion hybrids of SBA-16 functionalized by rare earth (Eu^{3+}, Nd^{3+}, Yb^{3+}) complexes of modified 2-methyl-9-hydroxyphenalenoe and 1,10-phenanthroline. J Solid State Chem 199:116–122
66. Guo XM, Wang XM, Zhang HJ, Fu LS, Guo HD, Yu JB, Carlos LD, Yang KY (2008) Preparation and luminescence properties of covalent linking of luminescent ternary europium complexes on periodic mesoporous organosilica. Microp Mesop Mater 116:28–35
67. Guo XM, Guo HD, Fu LS, Zhang HJ, Deng RP, Sun LN, Feng J, Dang S (2009) Novel hybrid periodic mesoporous organosilica material grafting with Tb complex: synthesis, characterization and photoluminescence property. Microp Mesop Mater 119:252–258
68. Sun LN, Mai WP, Dang S, Qiu YN, Deng W, Shi LY, Yan W, Zhang HJ (2012) Near-infrared luminescence of periodic mesoporous organosilicas grafted with rare earth complexes based on visible-light sensitization. J Mater Chem 22:5121–5127
69. Li Y, Yan B, Li YJ (2010) Sulfide functionalized rare earth (Eu/Tb) periodic mesoporous organosilicas (PMOs) hybrids with covalent bond: physical characterization and photoluminescence. Microp Mesop Mater 132:87–93
70. Li YJ, Wang L (2011) Photoactive rare earth hybrids covalently bonded to functionalized periodic mesoporous organosilica (PMO) by calix[4]arene derivative. J Mater Chem 21:1130–1138
71. Yan B, Gu YJ (2013) A novel white-luminescent ternary europium hybrids with phenanthroline functionalized periodic mesoporous organosilicas (PMOs) and 2-methyl-9-hydroxyphenalenone. Inorg Chem Comm 34:75–78
72. Sun LN, Zhang HJ, Peng CY, Yu JB, Meng QG, Fu LS, Liu FY, Guo XM (2006) Covalent linking of near-infrared luminescent ternary rare earth (Er^{3+}, Nd^{3+}, Yb^{3+}) complexes on functionalized mesoporous MCM-41 and SBA-15. J Phys Chem B 110:7249–7258
73. Yan B, Li QP (2014) Photofunctional hybrids of rare earth (Eu^{3+}, Tb^{3+})/beta-diketonate functionalized MCM-41/ SBA-15 mesoporous host prepared with 1,4,7,10-tetraazacyclododecane modified siloxane as covalent linkage. Microp Mesop Mater 196:284–291
74. Guo XM, Guo HD, Fu LS, Deng RP, Chen W, Feng J, Dang S, Zhang HJ (2009) Synthesis, spectroscopic properties, and stabilities of ternary europium complex in SBA-15 and periodic mesoporous organosilica: a comparative study. J Phys Chem C 113:2603–2610
75. Gu YJ, Yan B (2016) Eu^{3+}/Sm^{3+} hybrids based with 8-hydroxybenz[de]anthracen-7-one organically modified mesoporous silica SBA-15/16. Solid State Sci 50:9–17
76. Li YJ, Yan B (2011) Preparation, characterization and luminescence properties of the ternary europium complexes covalently bonded to titania and mesoporous SBA-15. J Mater Chem 21:8129–8136

77. Yan B, Li YJ (2011) Photoactive rare earth (Eu^{3+}, Tb^{3+}) centered hybrid systems with titania-mesoporous silica / aluminum mesoporous silica based hosts. J Mater Chem 21:18454–18461
78. Pang XL, Zhang HL, Yu XD, Wang T, Geng LJ, Wang YQ, Li YJ (2015) Synthesis and characterization of novel luminescent europium(III) hybrid materials with a host based on titania–mesoporous silica or alumina–mesoporous silica. RSC Adv 5:84790–84796
79. Fu LS, Ferreira RAS, Valente A, Rocha b LDC (2006) Optically functional nanocomposites with poly(oxyethylene)-based di-ureasils and mesoporous MCM-41. Microp Mesop Mater 94:185–192
80. Li YJ, Yan B (2009) Rare earth (Eu^{3+}, Tb^{3+})/beta-diketone modified mesoporous SBA-15/organic polymer hybrids: chemically bonded construction, physical characterization, and photophysical properties. Inorg Chem 48:8276–8285
81. Li YJ, Yan B (2010) Photoactive europium(III) centered mesoporous hybrids with 2-thenoyltrifluoroacetone functionalized SBA-16 and organic polymers. Dalton Trans 39:2554–2562
82. Li YJ, Yan B, Li Y (2010) Rare earth (Eu^{3+}, Tb^{3+}) centered mesoporous hybrids with 1,3-diphenyl-1,3-propanepione covalently linking SBA-15 (SBA-16) and poly(methylacrylic acid). Chem Asi J 5:1642–1651
83. Gu YJ, Yan B, Li YY (2012) Ternary europium mesoporous polymeric hybrid materials Eu(β-diketonate)$_3$pvpd-SBA-15(16): host-guest construction, characterization and photoluminescence. J Solid State Chem 190:36–44
84. Li Y, Wang JL, Chain W, Wang X, Jin Z, Lia XQ (2013) Coordination assembly and characterization of europium(III) complexes covalently bonded to SBA-15 directly functionalized by modified polymer. RSC Adv 3:14057–14065
85. Li Y, Zhu RD, Wang JL, Wang X, Liu SH (2015) Polyacrylamide modified mesoporous SBA-16 hybrids encapsulated with a rare earth (Eu^{3+}/Tb^{3+}) complex. New J Chem 39:8658–8666