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Luminescent materials of zeolite functionalized with lanthanides

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Abstract

Luminescent materials derived from the functionalization of zeolite with lanthanide (Ln^{3+}/zeolite) constitute intense research topic since such materials combine the attractive properties (*e.g.*, tunable morphology, high stability, and low cost) of zeolite and unique optical properties of Ln^{3+} ions (such as sharp and long-lived emission in the visible to NIR region with high color purity). Starting from a short summary on some preparation strategies of Ln^{3+}/zeolite, this highlight article reviews state-of-the-art research activities focusing on the improved visible and near-infrared (NIR) luminescence properties of lanthanide in these systems, the design and utilization of Ln^{3+}/zeolite as new building blocks for the fabrication of multicolor oriented zeolite thin film, transparent zeolite-polymer hybrid materials and luminescence sensors.

1. Introduction

Zeolites are microporous crystalline aluminosilicates consisting of [AlO_4] and [SiO_4] tetrahedra that are connected to form a network of channels and cavities where cations, water and/or small molecules may reside.[1-4] Zeolite crystals have been widely used in a broad spectrum of applications in catalysis, ion-exchange and separation, due to their unique porous properties.[5, 6] In recent years, they have attracted considerable interest for the preparation of novel materials designed at the nanosized level and they are of particular interest in the area of optical materials where pre-defined distances or a specific spatial pattern of the guests is required to obtain a desired optical response.[7-12] Especially, by the combination of the unique photophysical properties of Ln^{3+} ions (such as sharp and long-lived emission in the visible to NIR region with high color purity)[13-16] and attracting properties (*e.g.*, tunable morphology, high stability, and low cost) of zeolites, a variety of luminescent Ln^{3+}/zeolite host-guest materials are successfully prepared as new phosphors.[17-23] Up to now, the typical hosts used for Ln^{3+} ions or lanthanide complexes are two types of synthetic zeolites, including faujasite-type zeolite (*i.e.*

zeolite X and zeolite Y)[7, 20] and zeolite L.[11, 23-27] In addition, there have been a few reports on Ln^{3+}/zeolite A or ZSM-5-based host-guest materials.[22, 28-34]

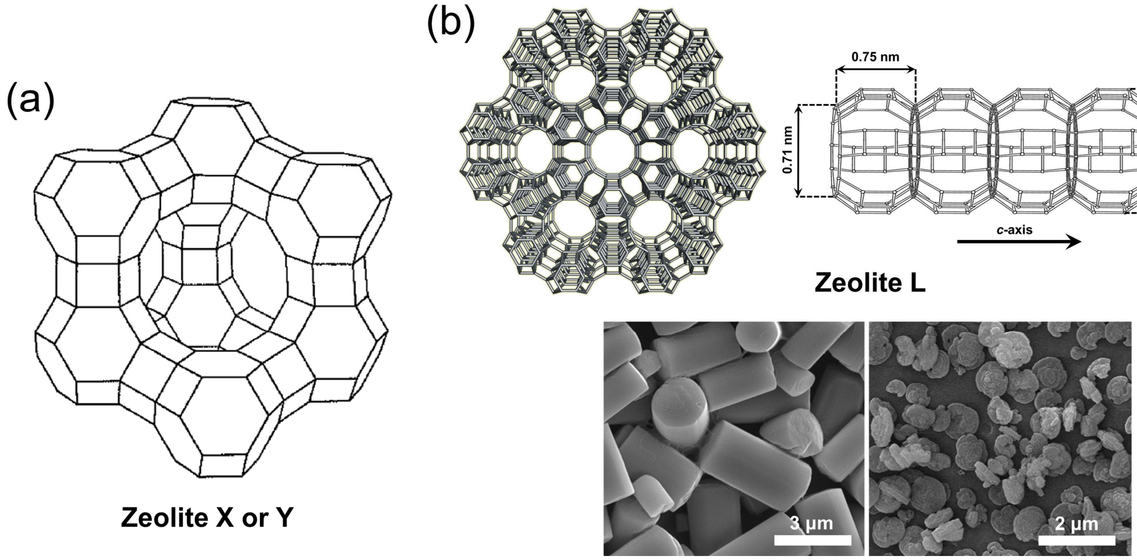

Fig. 1 (a) Framework of faujasite-type zeolite X or Y. (b) Structure and morphology of zeolite L. Top left: projection along *c*-axis, top right: side view of a 12-ring channel along the *c*-axis, down: scanning electron microscopy images of ZL crystals with elongated and disc shape.

Zeolites X and Y with the cubic faujasite (FAU) framework structure (Fig. 1a), are the most important zeolites for industrial applications, with two typical formulas: $Na_{86}[(AlO_2)_{86}(SiO_2)_{106}]\bullet 264H_2O$ for zeolite X and $Na_{56}[(AlO_2)_{56}(SiO_2)_{136}]\bullet 264H_2O$ for zeolite Y.[13] They are distinguished by their Si/Al ratio (Si/Al < 1.5 for zeolite X, Si/Al > 1.5 for zeolite Y) and consequently by their Na^+ content.[35] All zeolite frameworks can be built by linking in a periodic pattern that is the tetrahedron. As a primary building unit of zeolite, the tetrahedron depicted as $[SiO_4]$ and $[AlO_4]$ is formed by the center atoms (such as Si^{IV} and Al^{III}) with relatively low electronegativities and the oxygen atoms locating at the corners.[36] In term of zeolites X and Y, the tetrahedral connection of $[SiO_4]$ and $[AlO_4]$ produces a cubic FAU framework structure consisting of two different types of cages: the sodalite cage (β-cage) and the supercage (α-cage). The sodalite cage, with the internal diameter of 0.66 nm and square and hexagonal faces, is the basic building block of this zeolite. The supercage, which is the largest cage with the diameter of 1.2 nm, is created by eight sodalite cages.[37] The large channels and cavities of the faujasite structure allow for the adsorption of a relatively numerous organic molecules.[13] As a representative example of the early investigation, Kynast and co-workers[7] successfully achieved Ce^{3+}-doped zeolites X and Y and studied their optical properties in 1994. Efficient broad ultraviolet (UV)-emission with extremely high quantum yields up to 99% was observed for Ce^{3+} ion encapsulated in zeolites X and Y due to the allowed nature of the electronic f-d transitions within Ce^{3+} ion, thus opening exciting expectations for optical and medical applications.

Zeolite L (ZL) is a crystalline aluminosilicate in which corner-sharing $[SiO_4]$ and $[AlO_4]$ tetrahedra produce one-dimensional (1D) channels arranged in a hexagonal framework structure as shown in Fig. 1b.[38] These 1D channels, strictly parallel to the *c*-axis of ZL crystal, run through the whole crystal. The stoichiometry of ZL is $(M^+)_9[(AlO_2)_9(SiO_2)_{27}]\bullet nH_2O$, where M^+ are monovalent cations compensating the negative charge resulting from the aluminum atoms and n is 21 in fully hydrated materials and 16 at about 22% relative humidity.[39] The channels of ZL with a unit cell length of 0.75 nm have a smallest diameter of about 0.71 nm, and the largest internal diameter is about 1.26 nm. The distance between the centers of two channels is 1.84 nm. Each ZL crystal consists of a large number of channels, in which suitable guests can be incorporated. It has been synthesized in a size range starting from about 30 nm up to more than 20 μm as elongated, barrel, and disc-shaped crystals.[39] ZL was originally studied for catalytic applications.[4] Recently, it has attracted important interest as a host for preparing hybrid materials, and much research work on dye/ZL host-guest materials has been done by Calzaferri and co-workers.[38, 40] They have made significant contribution in studying their intriguing optical, photochemical, and photophysical properties.[10, 40-42] Through supramolecular organization of dyes into the channels of ZL, extremely high concentrations of monomeric dye molecules can be nicely achieved, owing to the geometrical constraint of the ZL framework.[38] In addition, the confined molecules can be well protected from chemical attack, photobleaching or thermal decomposition.[43] Furthermore, ZL crystals show a very important property of different reactivity between the base and the coat because of their hexagonal structure, which allows for the selective modification of base or coat by carefully designing the reaction conditions and using crystals with the right morphology.[40] Considering the merits of ZL crystals and encouraged by the promising results from Ln^{3+} species in other zeolites, we have developed a series of host-guest materials based on ZL crystals and Ln^{3+} species.[11, 23, 26, 44] The advantages of ZL instead of other zeolites and silica are: 1) the size of ZL crystal can be synthetically tuned from 30 nm to 20 μm with different morphologies, ranging from discs to elongated cylinders, for the use in different experiments, 2) the hexagonal structure of ZL crystal has strictly parallel one-dimensional channels, and 3) the facile functionalization the surface of ZL with targeting groups.

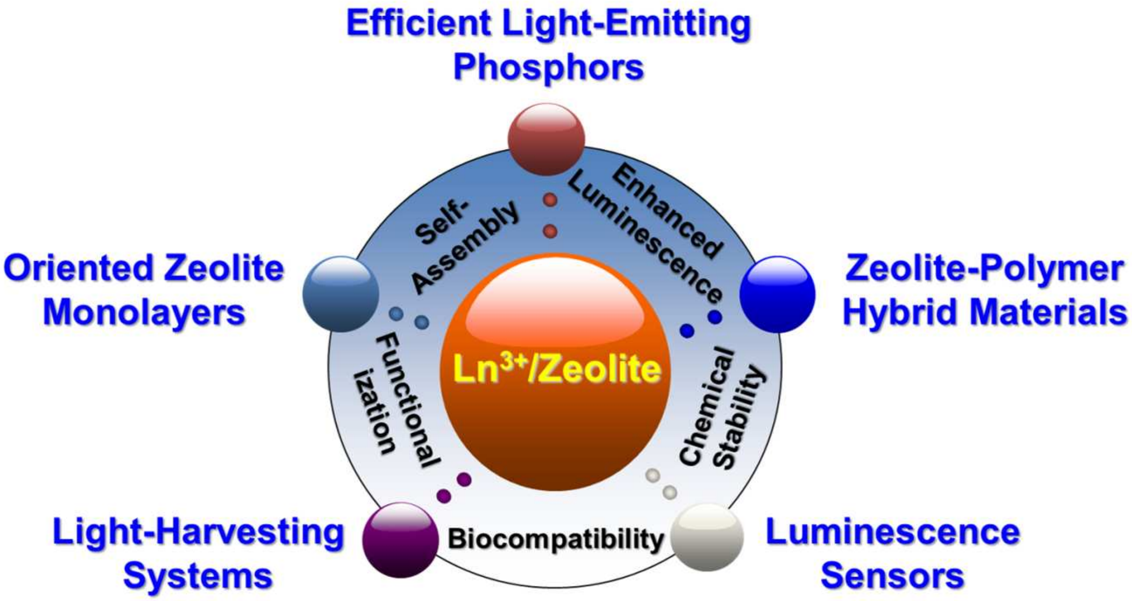

Fig. 2 Schematic illustration of Ln^{3+}/zeolite host-guest materials with unique properties for the construction of various hybrid systems.

In this review article, we present an overview of the preparation methods, luminescent properties and hybrid systems of host-guest materials obtained from Ln^{3+}-functionalized various microporous crystalline aluminosilicate crystals reported in the last two decades (Fig. 2). We firstly introduce how Ln^{3+}/zeolite materials can be prepared. Then we demonstrate the very distinguished luminescence performance of these materials and explain why the luminescent properties of Ln^{3+} species incorporated in zeolite crystals can be strongly improved in visible and NIR spectral regions. In view of the most research work contributing to the studies of luminescent properties of Ln^{3+}/zeolite host-guest materials, herein, we specially highlight the development of Ln^{3+}/ZL as versatile building blocks for the fabrication of multicolor oriented zeolite thin films, transparent zeolite-polymer hybrid materials and luminescence sensors in our laboratory. The microenviroment in the channels of ZL as well as its influence on the luminescence behavior of encapsulated lanthanide complexes have also been discussed. As an analogy of lanthanide-containing zeolite, lanthanide metal organic frameworks (LnMOFs) are an intensive research field and have been well summarized in several excellent reviews,[45-47] which are therefore not included in this review.

2. Preparation

The encapsulation of Ln^{3+} species into the cavities and channels of zeolite crystals can be achieved by ion exchange for only pure Ln^{3+} ions involved,[7, 48] or by direct physisorption method[27, 49] or an *in situ* synthesis inside the zeolite voids called "ship-in-a-bottle" method[17, 18, 20] for lanthanide complexes. Pure Ln^{3+}-exchanged zeolites can be easily synthesized by stirring a zeolite suspension in an aqueous solution containing an excess of lanthanide (III) salt (such as lanthanide nitrate or chloride) at a suitable pH at room temperature or under heating conditions.[50] Lanthanide ions can replace the exchangeable cations such as Na^+ or K^+ that compensate the negatively charged framework due to the isomorphical substitution of a silicon atom by an aluminum atom. Except for a few rare pure Ln^{3+}-exchanged zeolite samples with high luminescence quantum yields (QY),[7] most of them usually exhibit poor emission intensity owing to their low absorption efficiency resulting from the forbidden nature of the f-f transition of the Ln^{3+} ions, which leads to that they were used as a probe to obtain information on the structure and the environment inside the cages in which the cations are located rather than luminescent materials.[31, 49, 51-53] There have been some effective ways, such as co-doping diverse ions or calcination process after ion exchange, to strongly improve the luminescence efficiency of Ln^{3+}-exchanged zeolite.[26, 50, 54-58] Borgmann *et al*.[54] firstly described the phase transformation of Ln^{3+}/molybdate ions co-doped zeolite X into the highly luminescent sodalites with QY > 50% after the thermal treatment at 1000 °C. Normally, high temperature is demanded to produce high luminescence efficiency.

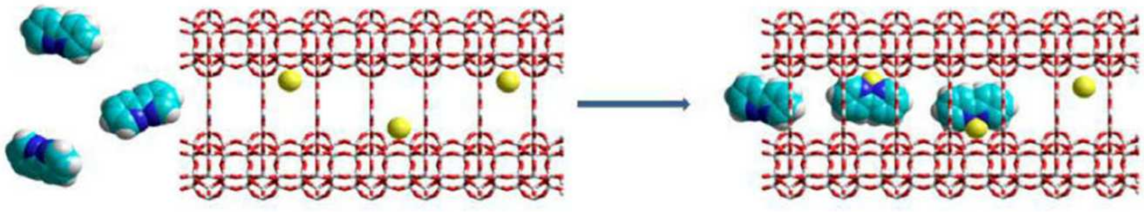

Fig. 3 Ship-in-a-bottle synthesis procedure used for the preparation of $Ln^{3+}(bpy)_n$-ZL host-guest materials; the yellow balls are Ln^{3+} ions.[11]

An alternative strategy, typically called "ship-in-a-bottle" method,[18, 59] is to *in situ* coordinate the Ln^{3+} ions confined in the cavities of Ln^{3+}-exchanged zeolites under the rigorous exclusion of moisture in a sealed container by the use of organic ligands with large molar absorption coefficients for improving the luminescence efficiency of Ln^{3+} *via* the so-called "antenna effect".[16, 60] This name is derived from an artistic bottle incorporating a ship that is bigger than the neck of bottle. In the field of chemistry, it means the *in situ* synthesis of compounds as guest materials confined in a host material. This can be achieved by inserting adequately small molecules and ions into the cavities of the host and then allowing further reaction until the product is too large to escape the cavities.[8] A variety of efficient light-emitting lanthanide complex/zeolite materials in visible and NIR regions have been synthesized in the different zeolite frameworks.[11, 17, 18, 20, 21, 61, 62] Wang *et al.*[11] prepared luminescent host-guest materials by insertion 2,2'-bipyridine (bpy) into the channels of Eu^{3+}/ZL and Tb^{3+}/ZL. The procedure is illustrated in Fig. 3. The lanthanide complexes $Eu^{3+}(bpy)_n$ and $Tb^{3+}(bpy)_n$ are formed in the channels of ZL, respectively. A large gain in luminescence intensity is observed after the incorporation of bpy due to the energy transfer from the bpy to Ln^{3+} ions. Most importantly, the encapsulated luminescent complexes show remarkably improved thermal stability. Upon heat treatment of $Tb^{3+}(bpy)_n$-ZL and pure $Tb^{3+}(bpy)_2Cl_3{\bullet}2H_2O$ complex in air at 400 ^oC for 4 h, the $Tb^{3+}(bpy)_n$-ZL host-guest material still displays the green emission with the characteristic four strong and narrow lines, while most of the narrow lines for the pure $Tb^{3+}(bpy)_2Cl_3{\bullet}2H_2O$ complex have disappeared. This indicates that the lanthanide complex inside ZL is stable up to 400 ^oC, but the pure $Tb^{3+}(bpy)_2Cl_3{\bullet}2H_2O$ complex has completely decomposed at 400 ^oC. Besides, pre-prepared lanthanide complexes can be directly incorporated into the cavities of zeolites by a facile physisorption method.[27, 49] Some representative samples of Ln^{3+}/zeolite host-guest materials achieved by above-mentioned preparation methods with different parameters including zeolite type, Ln^{3+} ions, co-doped ions, organic ligands, emission spectral region and QY are summarized in Table 1. The luminescence enhancement of Ln^{3+}/zeolite host-guest materials by some key influence factors will be discussed in more details as the following independent section.

Table 1 Representative samples of Ln^{3+}/zeolite host-guest materials achieved by different preparation methods and parameters.

Preparation method	Zeolite type	Ln^{3+} ions	Co-doped ions	Organic ligands[a]	Emission color	QY (highest, %)	Ref.
Ion exchange	ZX/ZY	Ce^{3+}	–	–	UV	99	7
	ZA/ZSM-5/ZY	Ce^{3+}/Tb^{3+}	–	–	green	–	63
	ZX	Tb^{3+}	–	–	green	–	48
	ZX	Eu^{3+}/Y^{3+}	MoO_4^{2-}	–	red	55	54
	ZX	Ce^{3+}/Tb^{3+}	–	–	green	85	50
	ZY	Eu^{3+}	–	–	red	–	64
	ZY	Nd^{3+}	Ag^{+}	–	NIR	–	57
	ZY	Er^{3+}	Bi^{3+}	–	NIR	–	65
	ZY	Er^{3+}/Yb^{3+}	Bi^{3+}	–	green/red	–	66
	ETS-10	Er^{3+}	–	–	NIR	–	67
	ZL	Eu^{3+}/Tb^{3+}	–	–	blue/green/red	61	26
	ZL	Eu^{3+}/Nd^{3+}	Bi^{3+}	–	red/NIR	67	55
Physisorption	ZY	Eu^{3+}	–	–	red	–	49
	ZY/ZL	Eu^{3+}	–	DBM	red	–	27
In situ	ZY/ZSM/mor	Eu^{3+}	–	bpy/btfa/phen/dpic	red	–	31
	ZY	Nd^{3+}	–	PMS	NIR	9.5	17
	ZX	Eu^{3+}/Y^{3+}	MoO_4^{2-}	–	red	55	54
	ZX	$Nd^{3+}/Y^{3+}/La^{3+}/Gd^{3+}$	WO_4^{2-}	–	NIR	–	19
	ZX	Eu^{3+}	–	ttfa/phen	red	–	18
	ZX	Eu^{3+}/Tb^{3+}	–	bzp/acbp	full-color	27.8	20
	ZL	Eu^{3+}/Tb^{3+}	–	bpy	green/red	–	11
	ZL	Er^{3+}	–	DFB	NIR	2.5	21
	ZL	Eu^{3+}	–	TTA/DBM/BPY/PHEN	red	79.3	23
	ZA	Eu^{3+}/Tb^{3+}	–	TTA/TAA	green/red/white	57.1	22

[a] DBM=dibenzoylmethane; btfa=benzoyltrifluoroacetone; phen=phenanthroline; dpic=dipicolinic acid; PMS=bis(perfluoromethylsulfonyl)amine; ttfa (TTA)=thenoyltrifluoroacetone; bzp=benzophenone; acbp=4-acetylbiphenyl; DFB=decafluorobenzophenone; TAA=1,1,1-trifluoroacetylacetone.

3. Luminescence enhancement of Ln^{3+}/zeolite in visible and NIR spectral regions

3.1 Thermal treatment

The luminescence efficiency of most purely Ln^{3+}-exchanged zeolite crystals is very low, for instance, quantum yield < 1% for pure Eu^{3+}-doped zeolite X.[18] Recent studies revealed that a low lying $O \rightarrow Eu^{3+}$ charge transfer (CT) transition of both hydrated and dehydrated samples are mainly responsible for the low efficiency, which strongly deactivates the excited state of Eu^{3+}, along with the low QY also partly resulting from the coupling of the Eu^{3+} $^5D_0$ state with high-energy vibrations of OH species, such as water molecules in the zeolite cavity.[13, 18] The enhancement of the luminescence by a suitable thermal treatment is generally attributed to the dehydration,[18] the migration of the Eu^{3+} ions from the supercages to the sodalite cages,[52] and the phase transformation to the sodalities.[19, 54] Interestingly, a strong and bright violet-blue emission color was observed upon irradiating the calcined Eu^{3+}/ZLs at 700 °C in air under UV light (Fig. 4a).[26] Emission spectrum reveals a strong broad band in the range of 350 to 450 nm with maximum at 409 nm, and almost no sharp emission lines due to the $^5D_0 \rightarrow ^7F_J$ (J=0-4) can be observed. The band appears when the samples are annealed at 300 °C and the intensity of which increases with the annealing temperature increasing from 300 to 700 °C. However, further increasing the temperature leads to a decreased intensity. The violet-blue emission band is attributed to Eu^{2+} resulting from the reduction of Eu^{3+} located in the channels of ZL. The presence of Eu^{2+} species in the channels of ZL has been confirmed by XPS as reported by Ding *et al*,[68] and they also found that the emitting color of the annealed Eu^{3+}/ZLs can be controlled by changing the solvents used in the washing step during preparation of the samples. Eu^{3+}/ZL crystals washed with deionized water or methanol followed by calcinations at 700 °C produce strong violet-blue emission (Fig. 4b), whereas washed with ethanol can make them bright red luminescence (Fig. 4c). The frameworks of ZLs play a vital role in protecting the Eu^{2+} species, since only red emission can be obtained when heating the sample at 1100 °C that cause the collapse of the framework of ZLs (Fig. 4d).

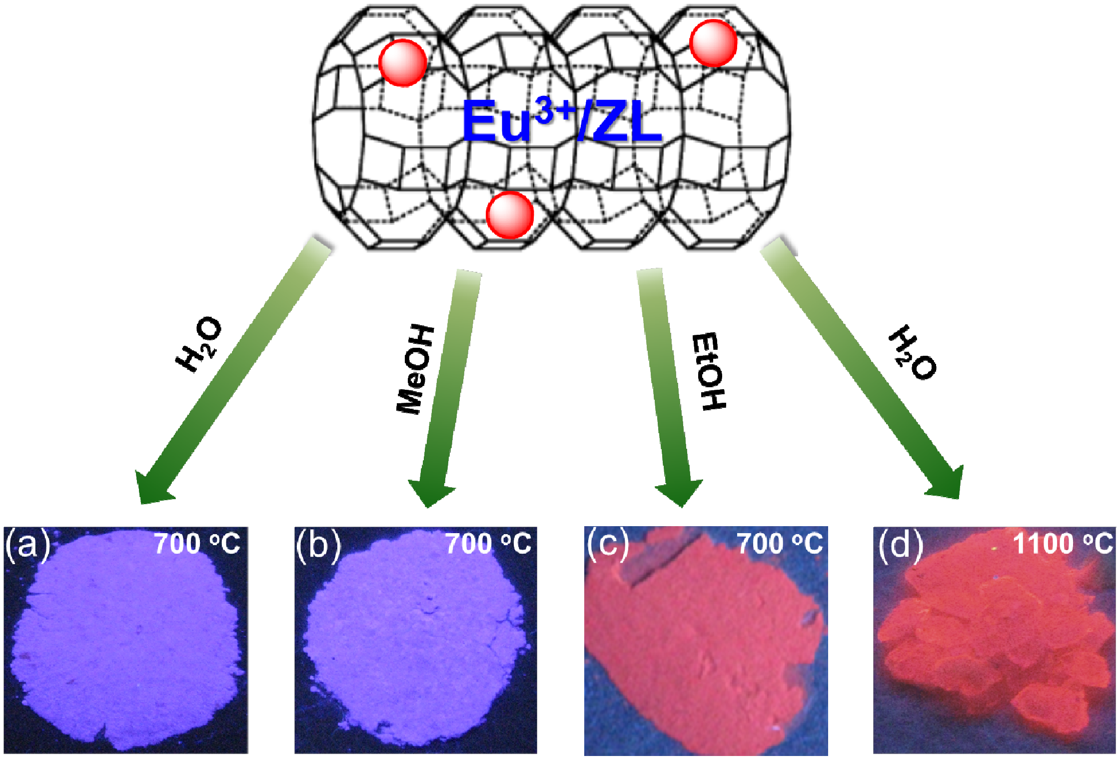

Fig. 4 Eu^{3+}/ZL samples washed by solvents and calcined at different temperature: (a) washed with H_2O and calcined at 700 ^{o}C, (b) washed with EtOH and calcined at 700 ^{o}C, (c) washed with MeOH and calcined at 700 ^{o}C, and (d) washed with H_2O and calcined at 1100 ^{o}C.

Near-infrared luminescent lanthanide materials, as efficient NIR light emitters, have presented considerable potential for applications in optoelectronics and telecommunication technologies. Although zeolite crystals have been used as excellent host materials for loading NIR Ln^{3+} ions, it is difficult to observe NIR luminescence for pure NIR Ln^{3+}-exchanged zeolites, owing to the intensive nonradiative relaxation of the excited states of the NIR Ln^{3+} ions by the water molecules confined in the zeolite cages.[13] However, upon calcination at high temperatures, microporous titanosilicate ETS-10 doped with Er^{3+} ions transforms into narsarsukite with strong NIR luminescence.[67] Mech *et al.*[69] recently reported an efficient NIR emission in the annealed Er^{3+}/ZL crystals, which is resulted from the energy transfer from the excited oxygen vacancies generated during the annealing processing. The emission can be finely excited in the whole near UV-VIS-NIR spectral range from 355 to 700 nm. This work shows us the first step toward versatile, zeolite-based NIR sources that can be excited with white light (Fig. 5).

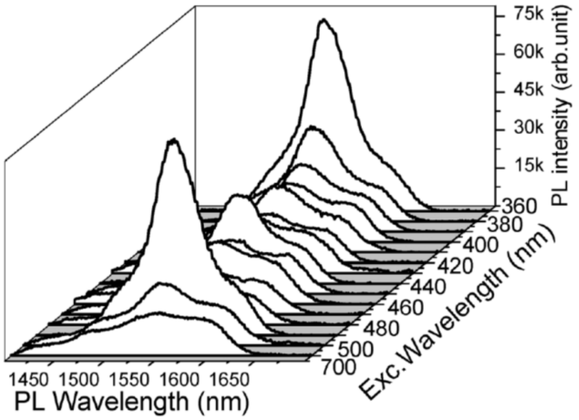

Fig. 5 NIR photoluminescence spectra of the annealed Er^{3+}/ZL sample recorded under Ti: Sapphire 360-700 nm excitation range, with a power pulse of 200 mW.[69]

Interestingly, Bai and co-workers[70] firstly observed a strong white-light emission from annealed pure zeolite Y crystals under ultraviolet light excitation. As shown in Fig. 6a, all samples exhibit broad emission bands covering the whole visible region, and the emission intensity of annealed zeolite samples increases by raising annealing temperature from 100 °C to 500 °C. Further increase of annealing temperature leads to the fast quenching of the emission (Fig. 6b). Meanwhile, the emission peak shifts from 495 nm to 530 nm, and then returns to 500 nm. The strongest emission intensity appears at the the annealing temperature of 500 °C with highest luminescence quantum yield of ~ 10% (Fig. 6b). Moreover, the emission lifetime monotonously increases from 223 μs to 251 μs with increasing annealing temperature from 100 °C to 700 °C. The origin of white-light emission is ascribed to oxygen vacancies formed during the annealing process. These new findings make the annealed zeolites as promising white-light emitting luminophores for solid-state lighting (SSL).

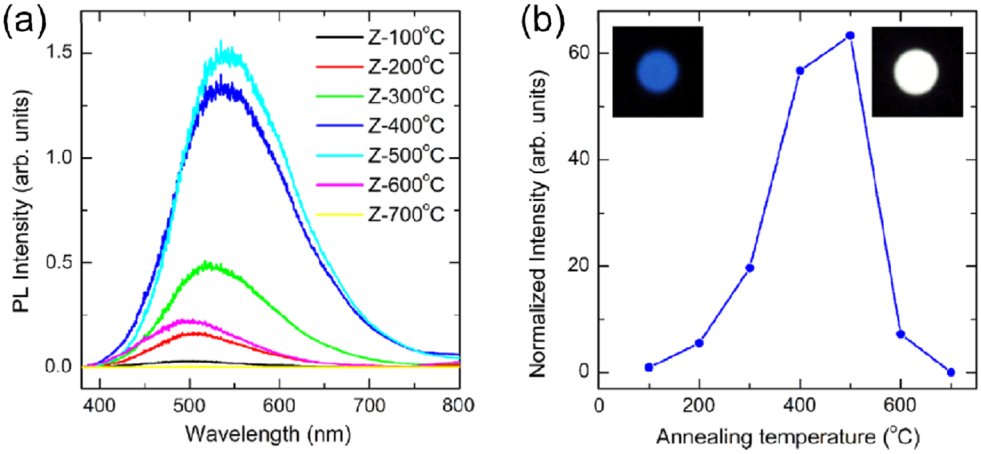

Fig. 6 (a) PL spectra of annealed zeolite Y at different temperatures upon excitation at 325 nm. (b) Normalized intensity at peak position as a function of annealing temperature with respect to that of Z-100 ^{o}C sample. The inset shows the photographs of the Z-100 ^{o}C (left) and Z-500 ^{o}C (right) samples excited by 325 nm with a power density of 2 mW/cm^{2}.[70]

3.2 Co-doping ions

Despite thermal treatment of Ln^{3+}-exchanged zeolites, the total luminescence output remains relatively low, owing to their weak absorption efficiency arising from the forbidden nature of the f-f transition of Ln^{3+} ions. In order to enhance luminescence from Ln^{3+}/zeolites, various ions, such as Ce^{3+},[50, 63] metalates (*e.g.*, MoO_4^{2-} and WO_4^{2-}),[19, 54] Ag^{+},[57] and Bi^{3+},[55, 65, 71] have been co-doped into the Ln^{3+}-functionalized zeolites. By heat-treatment, the obtained multicomponent ions co-doped zeolites can be converted into efficient luminescent materials showing strong luminescence. Recently, energy transfer between Ce^{3+} and Tb^{3+} in zeolite X has been extensively studied by Kynast and co-workers.[50] The Ce^{3+} ion can transfer the excitation energy to the Tb^{3+} ion with the energy transfer efficiency about 90% after the strong absorption of 254 nm light. The highest QY of 85% for Tb^{3+} emission sensitized by Ce^{3+} can be achieved by excitation at 330 nm. Energy transfer from $Ce^{3+}\rightarrow Tb^{3+}$ can also take place in zeolite Y, whereas no evidence for energy transfer can be found in ZSM-5 and zeolite A.[63] In addition, co-doping Eu^{3+} and Tb^{3+} in the same zeolite Y matrix followed by the thermal treatment at 800 ^{o}C has demonstrated the multicolor luminescence, including blue (434 nm), green (543 nm), and red (611 nm) colors.[72] This luminescent material may give rise to potential applications in white light-emitting devices and erasable optical storage.

As well known, owing to all inorganic bismuth compounds with a low melting point, bismuth-related dissociation reactions in zeolite cages can happen upon calcination at a high temperature.[73] Moreover, bismuth compounds tend to form agglomerates owing to bismuth migration in zeolite cages or channels. When the samples are suddenly cooled down, the agglomerates can act as blocks for selectively closing down the "in-out windows" of water molecules, *i.e.* Ln^{3+} can be sealed in a low-vibrational environment by bismuth agglomerates, which leads to strong and long-lived visible and NIR emissions.[65, 71] Sun *et al.*[65] demonstrated that highly efficient and air-stable NIR (1531 nm) emission from annealed erbium/bismuth co-doped zeolite Y crystals with long luminescence lifetime of 4.2 ms at 1531 nm, which may be due to some Er^{3+} ions sealed completely in the sodalite cages and hexagonal prisms through bismuth agglomerates after thermal treatment of samples at 830 °C and water molecules mostly existing in the supercages without chance to interact with them (Fig. 7a). The results clearly revealed that efficient NIR emission can be achieved at atmospheric circumstance by effectively separating Ln^{3+} ions from coordinated water in porous zeolite hosts, even a large number of water molecules trapping in the samples. Similarly, Li and co-workers[55] observed a strong red emission and NIR emission from annealed Ln^{3+} (Ln=Eu, Nd) and Bi^{3+} co-doped zeolite L crystals at 700 °C (Fig. 7b). Photoluminescence studies reveal a lifetime of 1.93 ms and a $^5D_0$ quantum efficiency (QY=66.98%) for Eu^{3+} in the Eu^{3+}/Bi^{3+}-ZL when excited into the absorption line of Eu^{3+} at 395 nm. Besides, a longer lifetime of 0.196 ms for Nd^{3+} in the annealed Nd^{3+}/Bi^{3+}-ZL has been obtained compared to values for Nd^{3+} in the other zeolite host. Furthermore, the morphology and size distribution of ZL crystals are well-kept during the synthetic process. The presented results show an important rational strategy for the design of strongly visible and NIR-emitting zeolite-based materials, and these findings may pave the way for the applications of Ln^{3+} ions doped zeolite materials in different optical devices.

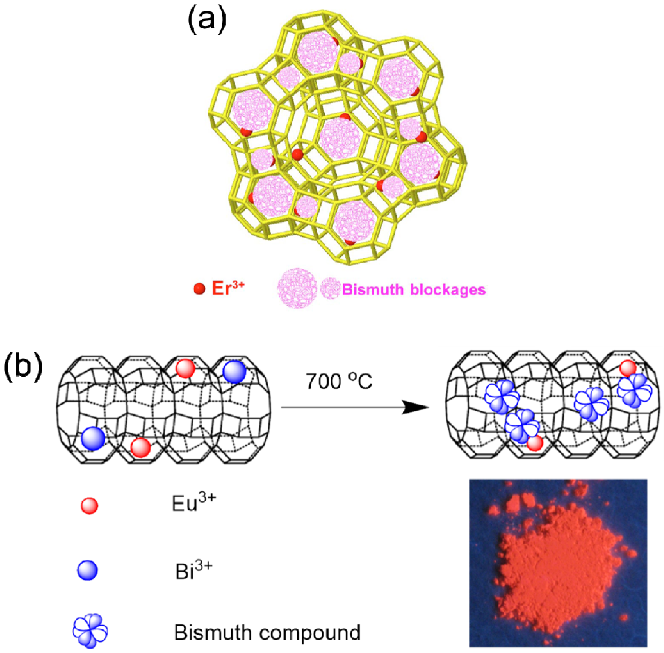

Fig. 7 (a) Schematic drawing of the structure of Er^{3+}/Bi^{3+} co-doped zeolite Y crystals annealed at high temperatures.[65] (b) Synthetic strategy of preparation of Eu^{3+}/Bi^{3+}-zeolite L luminescent materials with digital photo under UV irradiation (λ_{max}=365 nm).[55]

Very recently, the upconversion (UC) fluorescence properties of Bi/Er/Yb co-doped zeolite Y crystals are investigated by Bai and co-workers.[66] Intense green and red emissions with emission peaks at 532 nm, 554 nm and 664 nm are simultaneously observed at room temperature. It is revealed that the UC emissions can be well tuned by the change of Yb^{3+} concentration in zeolites. With the increase of Yb^{3+} concentration, the green and red emissions are enhanced about 5 and 243 times, respectively. Moreover, the intensity ratio of red-to-green emission is increased from 0.26 to 12.2. The tuned emission originates from an energy back transfer from Yb^{3+} to Er^{3+} ions. It is expected that the resulting intense single band red emission of the Bi/Er/Yb co-doped zeolites will provide potential application for *in vivo* bioimaging.

3.3 Sensitized luminescence with organic molecules

The optical transitions of the lanthanide Ln^{3+} ions involve 4f orbitals which are strongly shielded from the chemical environment by $5s^2$ and $5p^6$ electrons. The f-f transitions are parity forbidden, which results in very small absorption coefficients and slow emissive rates, as well as long-lived excited states and line-like emission bands. As a consequence, it is unfavorable to directly excite the Ln^{3+} ions.[11, 16] To overcome the difficulties of low light absorption of Ln^{3+} ions, a variety of organic ligand molecules as light collectors with large molar absorption coefficients have been introduced to sensitize Ln^{3+} ions for greatly intensifying their typical emissions through the so-called "antenna effect",[13, 60] which is a light conversion process by means of an absorption→energy transfer→emission sequence involving distinct absorption by a ligand (light collector) and emission by a Ln^{3+} ion (light emitter).[22] The encapsulation of organic sensitizers within diverse Ln^{3+}-exchanged zeolites has frequently been achieved by means of the *in situ* synthetic strategy, typically called "ship-in-a-bottle" method.[11, 17, 20, 22, 31] Strong sensitized luminescence of lanthanide complex/zeolite host-guest materials has been attained due to the effective energy transfer from organic ligands to Eu^{3+} or Tb^{3+} or both Eu^{3+} and Tb^{3+} ions simultaneously within the zeolite crystals. Consequently, the emission colors of the host-guest materials can be finely tuned by changing the relative amounts of the Eu^{3+} and Tb^{3+} ions in the zeolite hosts. Wada *et al.*[20] succeeded in fine control of red-green-blue (RGB) photoluminescence from Eu^{3+}/Tb^{3+}-exchanged faujasite-type zeolites by changing the amounts and ratios of Ln^{3+} ions and the nature of the photosensitizers (benzophenone or 4-acetylbiphenyl). Figure 8a demonstrates how the emission from such host-guest materials can be tuned through energy transfer process between sensitizer molecules and Ln^{3+} ions for giving full-color performance. The emission intensity can also be tailored by the change of excitation wavelength or the temperature. Ding *et al.*[62] loaded 4-fluorobenzophenone (FBP) molecules into the channels of Ln^{3+}/ZL (Ln=Eu, Tb or both Eu and Tb) through the gas diffusion method to achieve luminescent host-guest materials. Strong sensitized luminescence has been obtained due to the effective energy transfer from FBP to Eu^{3+} or Tb^{3+} or both Tb^{3+} and Eu^{3+} simultaneously within the crystal channels. As a consequence of this, the emitting colors of the host-guest materials can be tuned by changing the relative amounts of the Eu^{3+} and Tb^{3+} ions in the ZL microcrystals (Fig. 8b). They also prepared host-guest materials, Eu^{3+}(tta)$_x$/ZL and Eu^{3+}(tta)$_x$(phen)$_y$/ZL, by gas insertion of tta as well as tta and phen within the channels of Eu^{3+}/ZL, respectively. The lifetime of Eu^{3+} is shown to be longer than the Eu(tta)$_3$.3H$_2$O complex, which is attributed to the inhibition of the nonradiative deactivation pathways by confinement in the nano-cavities or channels of zeolites. Furthermore, improved photostability has been observed.

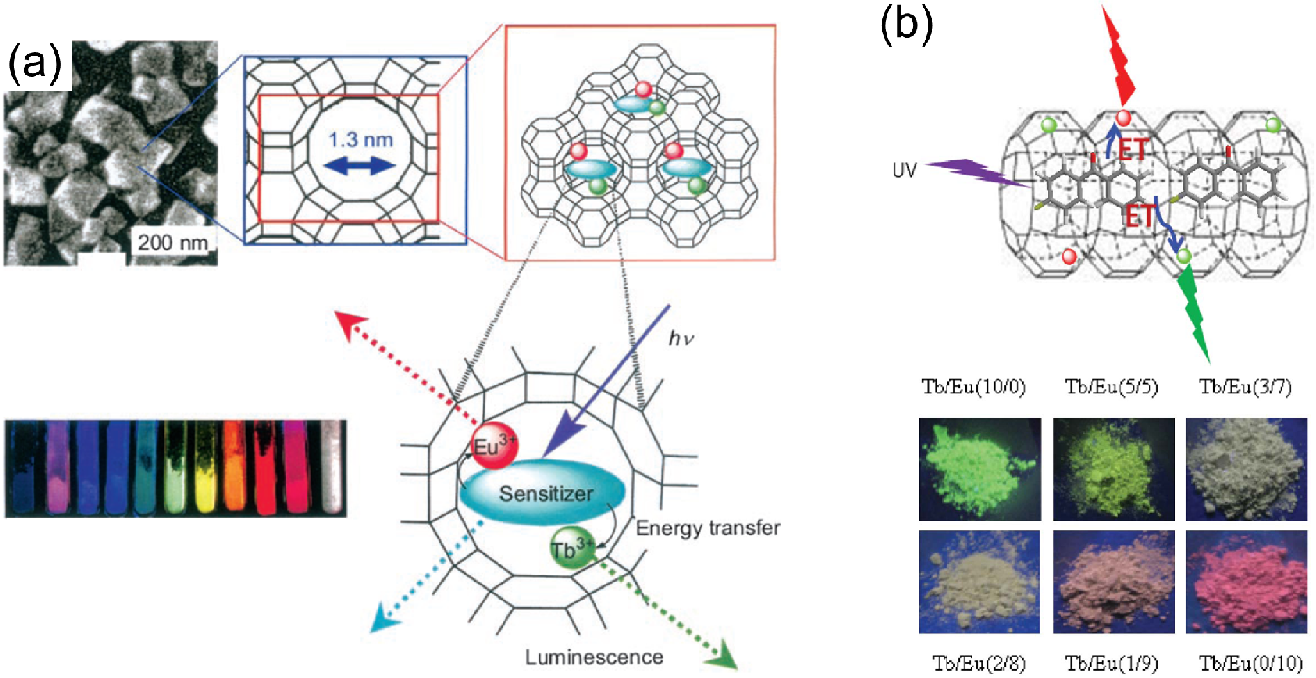

Fig. 8 (a) Schematic diagram showing the mechanism for energy transfer process between sensitizer molecules and Ln^{3+} ions for giving full-color performance depending on the incorporated amounts of Tb^{3+} and Eu^{3+} ions, the type of photosensitizers (benzophenone or 4-acetylbiphenyl), and the excitation wavelength.[20] (b) Sensitized luminescence of Eu^{3+}and Tb^{3+} ions through energy transfer from FBP molecules with photographs of multicolor photoluminescence from the samples under UV irradiation (λ_{max}=254 nm).[62]

Er^{3+}-doped materials are of high importance in optoelectronics and telecommunications because the unique intra-4f transition $^4I_{13/2}\rightarrow{}^4I_{15/2}$ around 1.54 μm corresponds to the window of minimum attenuation in the silica-based optical fibers widely used in optical communications.[74] However, the weak light absorption ability of Er^{3+} ions leads to inefficient emission from 4f levels under direct excitation. The sensitization via the antenna effect for Er^{3+} is not as effective as for Eu^{3+} and Tb^{3+}

emitting in visible region because Er^{3+} ions are particularly susceptible to vibrational deactivation from high-energy oscillators, such as C-H and O-H bonds typically contained in the ligand, coordinated solvents and moisture.[75] It has been accepted that halogenated organic ligand can significantly increase the quantum yield of the NIR emission of the complex. Nevertheless, the presence of halogenations in organic ligands normally is detrimental for the structural stability of the complex.[24] Mech and his co-workers have developed an alternative to overcome the limitations (Fig. 9).[21] They inserted decafluorobenzophenone (DFB) within the channels of Er^{3+}/ZL crystals, which produce effective luminescence around 1.54 μm with a longer lifetime of 0.21 ms *via* "antenna effect", which is much longer than that obtained by using partially fluorinated benzophenes as reported by the same group.[24] The importance of this approach is that it can produce effective NIR luminescence without the formation of stable complexes.

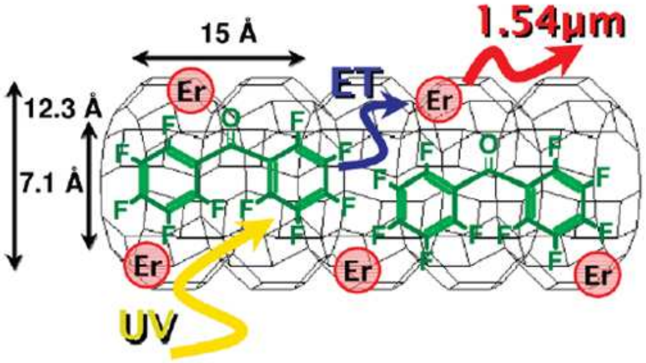

Fig. 9 Sketch showing the dimension of the ZL, and schematic illustration of the energy transfer between DFB and the Er^{3+} ions inside the nanochannel of ZL.[21]

The insertion of organic normally was carried out under the rigorous exclusion of moisture in a sealed container. Li *et al.*[76] recently reported a facile and effective way to improve the luminescence intensity of Eu^{3+}/ZL crystals by simple surface modification of them with silylated molecules (TTA-Si) consisting of a reactive siloxane group and a light absorbing moiety with the ability to coordinate and sensitize Eu^{3+} ions. The modification can easily be achieved by heating the mixture of Eu^{3+}/ZL crystals suspended in THF solution in which TTA-Si is dissolved. The strong luminescence was attributed to the formation of complexes between Eu^{3+} and tta moieties, most of which are located at the entrances of the nanochannels due to the linkages derived from the nucleophilic substitution of the terminal triethoxy groups of TTA-Si by the surface hydroxyl groups on ZL crystals. They observed that the photoluminescence emission intensity, $^5D_0$ lifetime, $^5D_0$ radiative (k_r) probabilities and the $^5D_0$ quantum efficiency (*q*) of Eu^{3+} increase as the aspect ratio (length to diameter ratio) the ZL crystals decreases. Furthermore, Li's group reported that new luminescent host-guest materials exhibiting tunable emission colors, upon the change of the excitation wavelength, have been achieved by surface modification of terbium (III) bipyridine-loaded zeolite L crystals with the ionic europium (III) complexes.[77] These obtained materials can be used as solid-state luminophores for UV-emitting LEDs because they can be excited in the near UV region.

3.4 Understanding the microenvironment in cages of zeolite crystals

The microenvironment in cages of zeolite crystals actually has a significant influence on the photophysical properties of the encapsulated lanthanide complexes, for instance, Ln^{3+}-exchanged zeolite typically possesses Bronsted acid sites owing to cation hydrolysis reaction,[78] which results in that most of the complexes are unstable and tend to decompose under such acidic conditions.[13] Thus, understanding and tuning the microenvironment inside the cavities of zeolite crystals is highly important to achieve optimal luminescence properties of zeolite-based materials. Until now, Li's group has made a large number of efforts to study them in detail.[23, 61, 79] Interestingly, they observed that the luminescence performances of $Eu^{3+}(tta)_x$-ZL and $Eu^{3+}(tta)_x(phen)_y$-ZL, including emission intensity, lifetime of Eu^{3+} and estimated quantum efficiency of Eu^{3+} $^5D_0$ excited stated, have increased significantly upon the treatment of them with ammonia gas (Fig. 10a).[61] They claimed the presence of NH_3 can promote the structural transformation of β-diketonate ligands from the *keto* form to the *enolate* one, the formation of complexes is thus favored. They also observed that the encapsulated europium (III) complexes in ZL crystals show remarkably increased photostability (Fig. 10b). Moreover, they investigated the acidity of Eu^{3+}-exchanged zeolite L (Eu^{3+}/ZL) and its influence on the luminescence performances of incorporated Eu^{3+}-β-diketonate complexes, including excitation and emission spectra, lifetime of Eu^{3+} ions, quantum yield, and energy transfer efficiency.[79] The acidity can hinder the formation of complexes between Eu^{3+} ions and tta molecules inside the ZL channels owing to the decomposition of Eu^{3+}-β-diketonate complexes under acidic conditions.

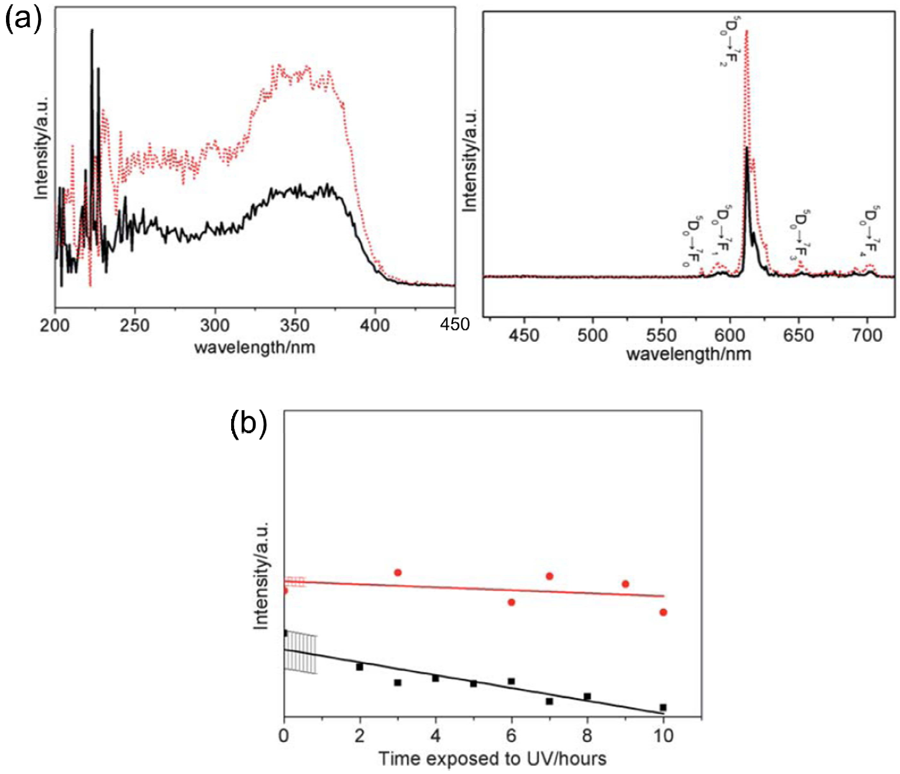

Fig. 10 (a) Excitation (left) and emission (right) spectra of Eu^{3+}(tta)$_x$(phen)$_y$-ZL host-guest material. (—) before treatment in ammonia gas atmosphere, (…) after treatment in ammonia gas atmosphere. Excitation spectra were observed at 612 nm and emission spectra upon excitation at 350 nm. (b) Changes of emission intensity at $^5D_0/^7F_2$ line under UV irradiation (λ_{max}=365 nm). Eu(tta)$_3$phen (■), Eu (tta)$_x$(phen)$_y$-ZL(●).[61]

Very recently, Li and co-workers[23] observed a surprising increase of the luminescence efficiency of Eu^{3+}-β-diketonate complexes loaded in the channels of nanosized zeolite L (NZL) crystals after modification with an imidazolium-based stopper molecule (Fig. 11). They elucidated the responsible mechanism by comparing two different diketonate ligands with different p*Ka* values and two aromatic imines (Bipy and Phen) and by using steady-state and time-resolved photoluminescence spectroscopy. The explanation of this luminescence enhancement is that the presence of the imidazolium-based stopper molecule is favorable to the sustainable formation of Eu^{3+}-β-diketonate complexes with high coordination by decreasing the proton strength inside the channels of NZL. The optical characteristics of the new luminescent host-guest materials could make them very promising for developing novel optoelectronic devices.

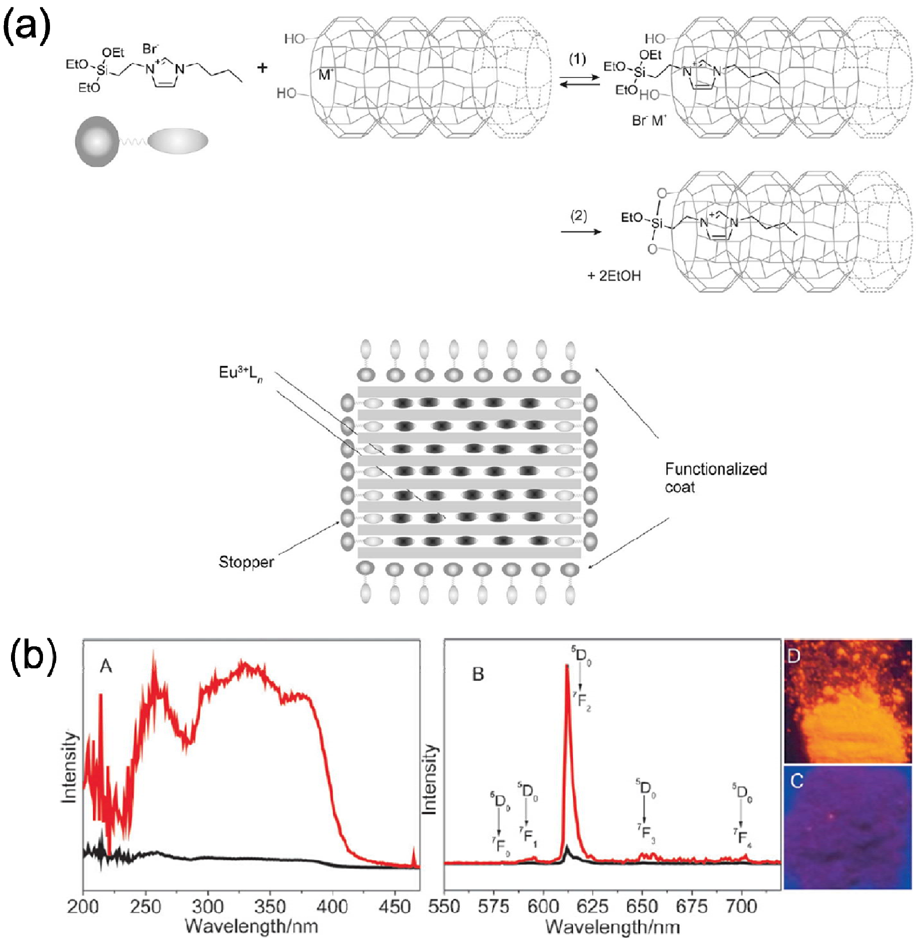

Fig. 11 (a) Upper: selective modification of the ZL channel entrance by (1) sonication and (2) reflux. Lower: stopper and coat functionalized NZL crystal loading inside Eu^{3+} complexes as guests. (b) Excitation spectra (A) and emission spectra (B) of $Eu^{3+}(TTA_n)$-NZL (black line) and ($Eu^{3+}(TTA_n)$-NZL)-1(1100) (red line). Excitation spectra were observed at 612 nm and emission spectra upon excitation at 345 nm. Photographs of the two samples taken under near UV excitation: (C) $Eu^{3+}(TTA_n)$-NZL and (D) ($Eu^{3+}(TTA_n)$-NZL)-1(1100).[23]

4. Oriented ZL monolayers with functional linkers

The controlled assembly of zeolite crystals into oriented structures is highly important for them to be applied to innovative materials and devices. One of the assemblies is oriented ZL monolayers, and therefore all of their channels are standing on different substrate such as quartz or glass. Another advantage of such monolayers is that the channels remain open on the side that is not blocked, thus leading to c-oriented open-channel monolayers (c-coMLs). Subsequent insertion of guest into the channels leads to materials with exciting properties, such as transfer of electronic excitation energy in one direction only.[41, 80] ZL monolayers can be achieved by covalently binding the crystals to a substrate,[81-84] by using coordination bonding,[85] or by microcontact transfer printing.[86-88]

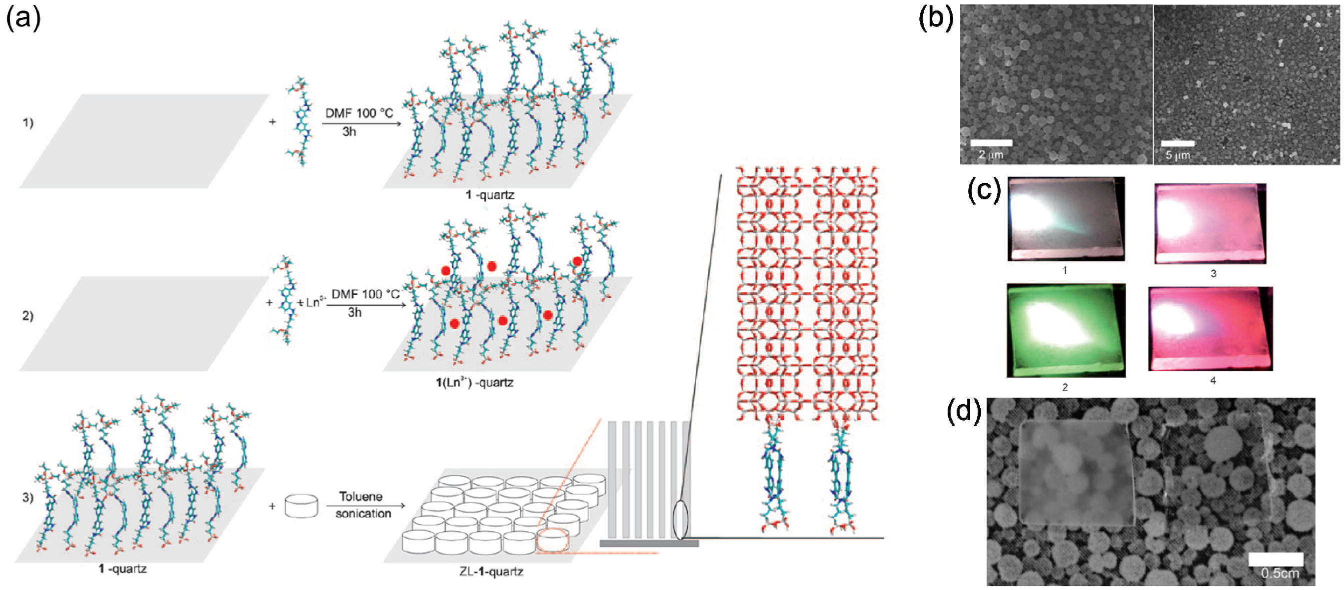

Fig. 12 (a) Schematic drawing of assembling ZL crystals into luminescent ZL monolayer with a functional linker **1**. (b) SEM images of a ZL monolayer at different magnification. (c) Photographs of such a monolayer upon UV excitation at 1) 270 nm, 2) 300 nm, 3) 340 nm, and 4) 365 nm.[44] (d) Photographs of a ZL-(TTA-Eu)-quartz monolayer. Left: uncoated monolayer, right: similar sample coated with PVA. The background is the SEM image of the layer.[89]

Molecular linkers are of high importance in obtaining such oriented ZL monolayer because they can bind and direct the arrangements and organization of zeolite crystals on substrates. Moreover, further adding functionalities such as luminescent properties to the molecular linker can open a much wider entry for fabricating chemical devices as the linkers can transfer electronic excitation energy between the outside and inside of zeolite crystal nanochannels.[90] Wang *et al.*[44] recently reported a strategy of achieving higher organization and luminescence in the oriented ZL monolayer by using a functional linker **1** that has the ability to coordinate and sensitize lanthanide ions[91, 92] and to self-assemble on substrate through hydrogen bonding (Fig. 12a). Dense, homogenous, well-oriented, stable and highly organized open channel ZL monolayers were thus obtained via this strategy by using triethoxysilylated bipyridine as the functional molecular linker (Fig. 12b). The emission color of the resulting layers can be finely tuned by changing the amount and type of Ln^{3+} ions coordinated with linker, by changing the guest inside the channels of ZL, and by changing the excitation wavelength (Fig. 12c). By utilization of the same strategy, Cao *et al.*[89] also succeeded in dense, well-oriented and emission color-tunable monolayers of ZL with highly ordered structure by using triethoxysilylated β-diketone[93, 94] as the functional linker. They observed that the degree of coverage and of dense packing become much higher upon introduction of Eu^{3+} ions to the substrate surface. The coordination of Eu^{3+} ion to the functional linker can favor the standing of the linker molecules on substrate, which can account for the improved quality of the obtained ZL monolayers. Oriented ZL monolayers are usually opaque or semitransparent and they therefore strongly scatter light in the visible region. Transparency is highly desirable for some applications in developing optical devices. Calzaferri *et al.*[43] realized the transparency by coating polymer of CR39 on the monolayer. Cao *et al.*[89] obtained transparent monolayers of ZL by coating the polymer PVA on the monolayers (Fig. 12d).

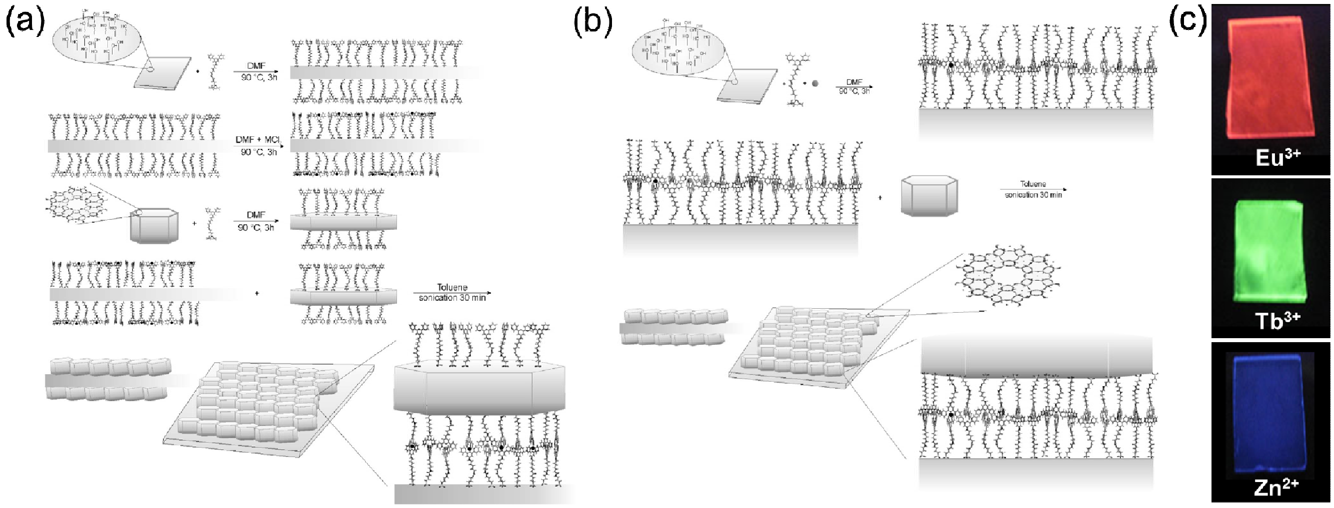

Fig. 13 Schematic illustration of (a) S-L(M) method and (b) S-(L-M-L) method for fabricating c-oriented ZL monolayers on a substrate.[85] (c) Photographs of the oriented ZL monolayers through the cooperative interaction of terpyridine and metal cations irradiated under UV irradiation (λ_{max}=254 nm).

As discussed above, oriented monolayers of ZL can be prepared by the use of molecular linkers through covalent binding. Functional linkers that can coordinate to and sensitize Ln^{3+} ions can allows both the realization of oriented ZL layers with improved qualities and the tunable luminescence of the obtained monolayers. The cooperative interactions between metal ions and terpyridine as a ligand have been widely used in the preparation of supramolecular assemblies that display appealing magnetic or luminescent properties, which has also been applied to prepare one-dimensional arrays of ZL crystals.[95] Li and co-workers[85] prepared oriented monolayer through the cooperative interaction of terpyridine and metal cations. They used two different strategies (*i.e.* S-L(M) method and S-(L-M-L) method) which lead to layers with different surface properties, as illustrated in Fig. 13a and b. The resulting layers display tunable emission colors depending on the coordinating cations (Fig. 13c). The self-assembly procedure is so versatile and robust that tailoring the properties of layers for meeting desired functionalities for a specific applications is possible. The study underlines the fascinating, advanced supramolecular organization that can be achieved by using coordination chemistry as a tool for self-assembling ZL crystals. A variety of applications can be envisaged, ranging from biology, diagnostics, optical and electro-optical devices, and photo electrochemistry to solar energy conversion.

5. Ln^{3+}/ZL materials for constructing transparent zeolite-polymer hybrid materials and luminescence sensors

The properties of Ln^{3+}/ZL host-guest materials outlined above make them very desirable for the development of various novel optical materials, such as lenses, infrared plastic light-emitting diodes (LEDs) for use in telecommunications, luminescent nanostructured materials for optical data storage, and also for improving chemical physical properties of polymers. Typically, for many of these optical applications, the Ln^{3+}/ZL host-guest materials have to be embedded in a polymer matrix without losing the transparency in the visible range. However, zeolite crystals usually tend to aggregate that gives rise to the light scattering in the visible range.[43] To overcome this drawback, Li *et al.*[96] carried out the surface modification of nanosized lanthanide complex-loaded ZL crystals for better dispersing in liquid monomer MMA (Fig. 14a). By polymerization, they achieved a novel transparent organic-inorganic zeolite-polymer hybrid material showing the characteristic emission of Ln^{3+} ion. The luminescence color of the transparent materials can be tuned by simply the kind of Ln^{3+} species located inside the channels of ZL (Fig.14b). They found that the PMMA polymer can protect the luminescence of Ln^{3+} species incorporated in the channels of ZL from water quenching. The obtained transparent organic-inorganic hybrid materials could be used to prepare different plastic photonic devices.

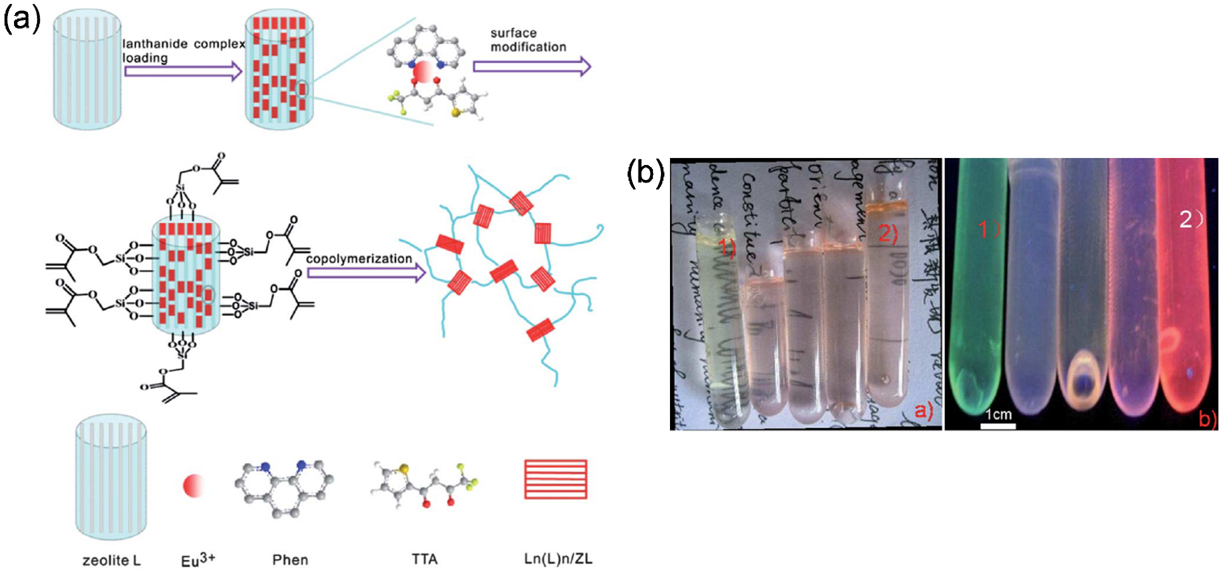

Fig. 14 (a) Procedure for preparing transparent and luminescent ZL-polymer hybrid materials. (b) Photographs of transparent and luminescent ZL-polymer hybrid materials. Left) under daylight; right) under UV irradiation; 1) material containing Tb^{3+} complexes, 2) material containing Eu^{3+} complexes.[96]

Normally, the leakage of guest species from the nanochannels of zeolite crystals occurs when the host-guest materials are used in solution since the inclusion of the guest species is a thermodynamically reversible process.[97] The same problem can still occur in lanthanide complex/zeolite host-guest systems, which hamper the further practical and optical applications of the materials in solution. Li and co-workers[25] designed and prepared a novel luminescent core-shell material by initial coating with polyelectrolytes and subsequent with a silica shell on the europium (III) complex $Eu(tta)_x$ loaded zeolite L microcrystals. Coating a silica shell on $Eu(tta)_x$/ZL crystals can prevent the leakage of tta molecules from the nanochannels of ZL crystals. Further functionalization of the silica-coated $Eu(tta)_x$/ZL crystals with non-luminescent terbium (III) complexes makes them as effective luminescent sensors for the detection of dipicolinic acid (DPA), *i.e.* an important molecular marker in spore-producing bacteria. The procedure is outlined in Fig. 15. In this case, the europium (III) complex inside the channel of ZL crystals encapsulated in the silica, as an internal calibration, is protected from the external influences such as solvents, providing a stable reference signals. Furthermore, they also reported the new luminescent core-shell composite composed of a dye (Coumarin 1)-loaded zeolite L nano-crystal and a silica shell with non-luminescent europium complexes immobilized on the surface.[98] The obtained core-shell composites were used as an ideal sensor for the ratiometric detection of DPA molecules at nanomolar concentrations.

As aforementioned, the luminescence of Eu^{3+}-β-diketonate complexes loaded in the channels of NZL shows strong positive response upon exposure to ammonia gas[23, 61, 79], which implies that these luminescent materials can be used as a potential sensor for detecting various alkaline molecules.

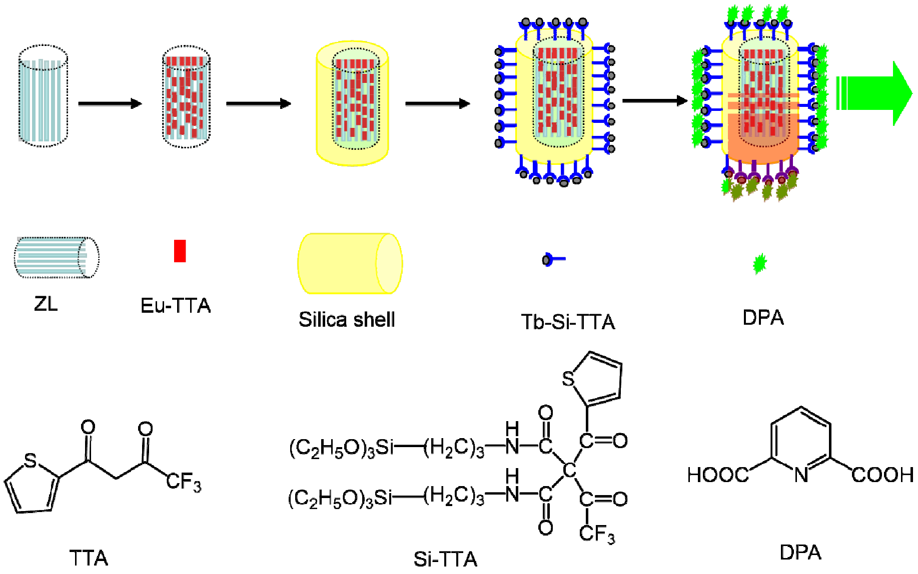

Fig. 15 Procedure for silica coating, surface modification of $Eu^{3+}(tta)_x$/ZLs and the use of them in DPA detection.

6. Conclusions and outlook

In summary, we have briefly reviewed the main research that is ongoing in the field of the functionalization of zeolite crystals with lanthanide, including preparation strategies and improved luminescence performance. We also highlighted the versatility and importance of ZL crystals as host materials for the preparation of luminescent host-guest materials with characteristic emission of lanthanide ions. The most interesting results obtained so far for Ln^{3+}-functionalized zeolite crystals are: 1) annealing Ln^{3+}-exchanged zeolites or Ln^{3+}/co-doped ions zeolites can lead to the luminescence enhancement; 2) strong NIR emission via white light excitation can be obtained in the annealed Er^{3+}/ZL; 3) incorporating lanthanide complexes inside the channels of zeolite crystals can improve their thermal stability and photostability which is highly important for the practical applications such as LED lighting; 4) multicolor emitting lanthanide complex-loaded zeolite host-guest materials can be achieved; 5) effective NIR luminescence without the formation of stable complexes in ZL crystals can be observed; 6) the luminescence efficiency of Eu^{3+}-β-diketonate complexes loaded in the channels of NZL crystals after modification with an imidazolium-based stopper molecule can be extremely increased; 7) highly ordered ZL monolayers with tunable luminescence properties can be obtained by using functional linkers that can coordinate to and sensitize Ln^{3+} luminescence; 8) transparent luminescent composites are available by embedding nanosized Ln^{3+}-functionalized ZL into the PMMA matrices; 9) luminescent core-shell materials can be used as an ideal sensor for the ratiometric detection of DPA molecules.

However, the study of this research topic is still in its infancy, efforts have been mainly focused on the preparation, morphology and luminescent properties. At least three key points should be taken into account in this research area in the near future: i) the composition and structure of the formed Ln^{3+} complexes inside the channels of zeolite crystals should be further clarified, which is highly important for us to understand the interaction between the host (zeolite crystals) and the guest (lanthanide complexes); ii) the oriented monolayers open the way for applications in biology, diagnostics and in optoelectronic applications, including artificial antenna systems, thin layer solar cells and light-emitting electrochemical cells (LEECs). However, the preparation of perfect monolayers on large substrate which are dense, homogeneous, well oriented remain a challenge task, which is a prerequisite for many technological applications; and iii) the applications of these novel host-guest should be further strengthen in various fields such as LED lighting (some of the materials can be excited by 395 nm and 465 nm together with their regular and tunable morphology), sensing, and luminescent solar concentrators (LSCs) for the production of cheaper solar electricity.

Acknowledgements

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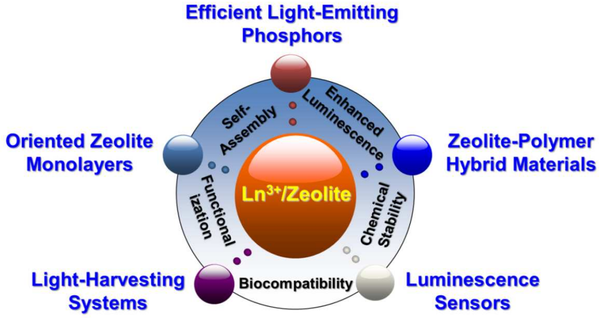
TOC



Luminescent materials derived from the functionalization of zeolite with lanthanide constitute intense research topic since such materials combine the attractive properties (*e.g.*, tunable morphology, high stability, and low cost) of zeolite and unique optical properties of Ln^{3+} ions (such as sharp and long-lived emission in the visible to NIR region with high color purity). This review highlights some examples to demonstrate that the utilization of zeolite indeed provides access to luminescent materials showing tunable luminescent performances, well-organized structures and useful host-guest interactions.

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Yu Wang received his PhD (2013) from City University of Hong Kong under the supervision of Prof. Andrey L. Rogach. Currently, he is working as a postdoctoral fellow at the Regional Centre of Advanced Technologies and Materials, Palacký University, Czech Republic. His research focuses on synthesis and optical spectroscopy of colloidal semiconductor nanocrystals, carbon dots, lanthanide-based functional materials, and their hybrid structures, for the study of light emission, self-assembly, charge transfer and energy transfer.

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