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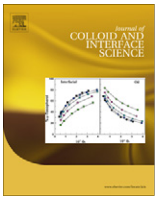

Lanthanide mesoporous SBA-15 hybrids through functionalized 6-hydroxybenz[de]anthracen-7-one linkage: UV–visible light sensitisation and visible-NIR luminescence

Yan-Jing Gu, Bing Yan *

Department of Chemistry, Tongji University, Siping Road 1239, Shanghai 200092, China
State Key Laboratory of Pollution Control and Resource Reuse, Tongji University, China

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A series of new visible and near-infrared (NIR) luminescent lanthanide-hydroxybenz[de]anthracen derivatives ($Ln(HBAN)_3(H_2O)_2(NO_3)_3$, $Ln(HBAN)_3phen(NO_3)_3$) were synthesized (HBAN-6-hydroxybenz[de]anthracen-7-one, Ln = Eu, Yb, Nd). Further, chemically bonded lanthanide hybrids of functionalized mesoporous silica (SBA-15) are prepared using HBAN-functionalized alkoxysilane (HBAN-Si) as linker, which is named as $Ln(HBAN\text{-}SBA\text{-}15)_3(NO_3)_3$, $Ln(HBAN\text{-}SBA\text{-}15)_3phen(NO_3)_3$ (Ln = Eu, Yb, Nd), respectively. The physical characterization and especially the photoluminescence properties for these hybrids are performed. SAXRD and BET of them revealed that all of these hybrid materials have uniformity in the mesostructure. 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.

1. Introduction

Lanthanide complexes have aroused intensive research efforts in view of their unique optical properties such as relative narrow emission band, large Stokes' shift, long luminescent lifetime, low luminescence quenching, and wide emission range covering near-infrared (NIR) region (e.g., Nd^{3+}, Yb^{3+}, Er^{3+}, Ho^{3+}) and visible-emitting region (such as Eu^{3+}, Tb^{3+}, Sm^{3+} or Dy^{3+}). However, lanthanide ions exhibit low luminescence intensity owing to the fact that their 4*f*–4*f* transitions are parity forbidden. One of the most useful strategies employed to overcome this drawback is to synthesize lanthanide coordination compounds of organic ligands acting as sensitizers, in which ligands absorb UV or visible light and efficiently transfer the energy to the central lanthanide ion through intramolecular energy transfer process and ultimately resulting in sensitized Ln^{3+} ion emission, so-called antenna effect [1,2].

Recently, a challenge in lanthanide coordination chemistry is to develop luminescent Eu^{3+} complexes that can be sensitized by visible light, which has become much important to satisfy the demand for less-harmful labeling reagents in the life sciences and low-voltage-driven pure-red emitters in optoelectronic technology. Meanwhile, much attention has been paid to near-infrared (NIR) luminescence of trivalent lanthanide ions for their promising application in the fields of bimolecular labels in luminescent bioassays [3,4], functional materials for optical telecommunication networks [5–7], and laser systems [8–10]. Candidates for luminescence in these spectral regions are trivalent ions of neodymium, praseodymium, samarium, dysprosium, holmium, erbium, and ytterbium. While a large extent to limit the practical applications of NIR-luminescent lanthanide complexes is due to their poor thermal stabilities and low mechanical strength [11,12], in the past few years, it has been recognized that the combination of lanthanide complexes and inorganic networks with good thermal and mechanical property using sol–gel synthetic route allows these drawbacks to be successfully circumvented [13,14]. Especially, the chemically bonded lanthanide sol–gel hybrid materials can avoid phase separation, inhomogeneous dispersion, and optical quenching, which easily occurs in the physical mixed sol–gel hybrids through the weak interactions between lanthanide complexes and silica moieties [15,16]. The mesoporous molecular sieves (MMSs) were used as a carrier for lanthanide complexes because of their novel and unique properties, such as rigidity, photostability, and well-defined hydrophilic/hydrophobic phase separation allowing for more sophisticated tuning of the microenvironment around lanthanide complexes [17,18]. Among SBA-15, as a host material for lanthanide complexes appears to be more attractive than other mesoporous silica for its large uniform pore size (up to 30 nm), thick silica wall, good stability, and so on [19,20].

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* Corresponding author.
E-mail address: byan@tongji.edu.cn (B. Yan).

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Lanthanide materials excited with visible light are more favorable than ultraviolet-excitable materials, for which they can avoid the disadvantages (low brightness and high-cost) of the ultraviolet light as the excitation and then the long-wave excitation strongly reduces both the background fluorescence and the interferences by inner filter effects due to the light absorption [21,22]. So in this article, we have synthesized organic ligand, 6-hydroxybenz[de]anthracen-7-one (HBAN) and its binary and ternary hybrids materials, $Ln(HBAN)_3(H_2O)_2(NO_3)_3$, and $Ln(HBAN)_3phen(NO_3)_3$ (Ln = Eu, Yb, Nd). Furthermore, HBAN was functionalized with organosilane (named as HBAN-Si), which played double roles of not only coordinating with lanthanide ions but also acting as an organosilane precursor to synthesize the functionalized mesoporous SBA-15 hybrid materials ($Ln(HBAN\text{-}SBA\text{-}15)_3(NO_3)_3$ and $Ln(HBAN\text{-}SBA\text{-}15)_3$ $phen(NO_3)_3$ (Ln = Eu, Yb, Nd)). Full characterization and detailed studies of the luminescence properties (upon excitation with visible light) of all synthesized materials were investigated.

2. Experimental section

2.1. Chemicals

2-Methoxynaphthalene, benzoyl chloride, aluminum chloride ($AlCl_3$), diluted hydrochloric acid (HCl), and methylene chloride (CH_2Cl_2) are from Aladdin. Pluronic P123 ($EO_{20}PO_{70}EO_{20}$ and tetraethoxysilane (TEOS) are from Aldrich. Cetrimonium bromide (CTAB) and 3-(triethoxysilyl)-propylisocyanate (TEPIC) are from Lancaster. 1,10-Phenanthroline (phen) is purchased from Sinopharm chemical reagent. $Ln(NO_3)_3{\cdot}6H_2O$ (Ln = Eu, Sm, Nd, Yb) were received by dissolving their respective oxides (Eu_2O_3, Sm_2O_3, Nd_2O_3 and Yb_2O_3) in concentrated nitric acid (HNO_3). The solvents ethanol, 1, 2-dichloroethane and tetrahydrofuran (THF) are used without treatment.

2.2. Synthetic procedures

2.2.1. Synthesis of 6-hydroxybenz[de]anthracen-7-one (HBAN)

HBAN was synthesized by the method in Ref. [23]. Equivalent molar mass of 2-methoxynaphthalene (10.000 g, 0.063 mol) and benzoyl chloride (8.856 g, 0.063 mol) was dissolved in 1,2-dichloroethane; meanwhile, aluminum chloride (8.4 g, 0.063 mol) was added into the solution and refluxed for overnight. Iced hydrochloric acid was used to decompose the reaction mixture, and the organic layer was washed by water and dried by sodium sulfate. Removing the solvent and greatly mixing with aluminum chloride (25 g), the container is placed into an oil bath, which is already preheated to 180 °C. The reaction mixture was maintained at this temperature for an hour with stirring and then poured into an iced hydrochloric acid. CH_2Cl_2 was used for the extraction, washed the organic layer with water, and dried by sodium sulfate. The solution was treated with rotary evaporator to remove the solvent. After being sublimed from ethanol, yellow needles products are obtained. Yield 82%. Elemental data: Anal. Calcd. for $C_{17}H_{10}O_2$ (246.26): C 82.91, H 4.09; Found: C 83.18, H 3.96. ^1H NMR: ($CDC1_3$, Me_4Si): δ15.73 (H, s, OH), δ7.20–8.70 (m, 9H). ^{13}C NMR: ($CDC1_3$, Me_4Si): δ109.1–140, δ169.9 (COH), δ185.9 (C=O). These data demonstrate the precursor had been synthesized successfully.

2.2.2. Synthesis of Ln^{3+} binary and ternary complexes (denoted as $Ln(HBAN)_3(H_2O)_2(NO_3)_3$/$Ln(HBAN)_3phen(NO_3)_3$, Ln = Eu, Nd, Yb)

$Ln(NO_3)_3{\cdot}6H_2O$ was dissolved in ethanol then add into the just enough HBAN to the above solution, and the molar composition of was controlled as 1:3, stirring at room temperature for 12 h, finally received Ln^{3+} binary complexes, which proved to be $Ln(HBAN)_3(H_2O)_2(NO_3)_3$. The same method was used to prepare ternary complexes, with the molar ratio of Ln^{3+}: HBAN: phen being 1:3:1, then obtained $Ln(HBAN)_3phen(NO_3)_3$. Elemental analysis

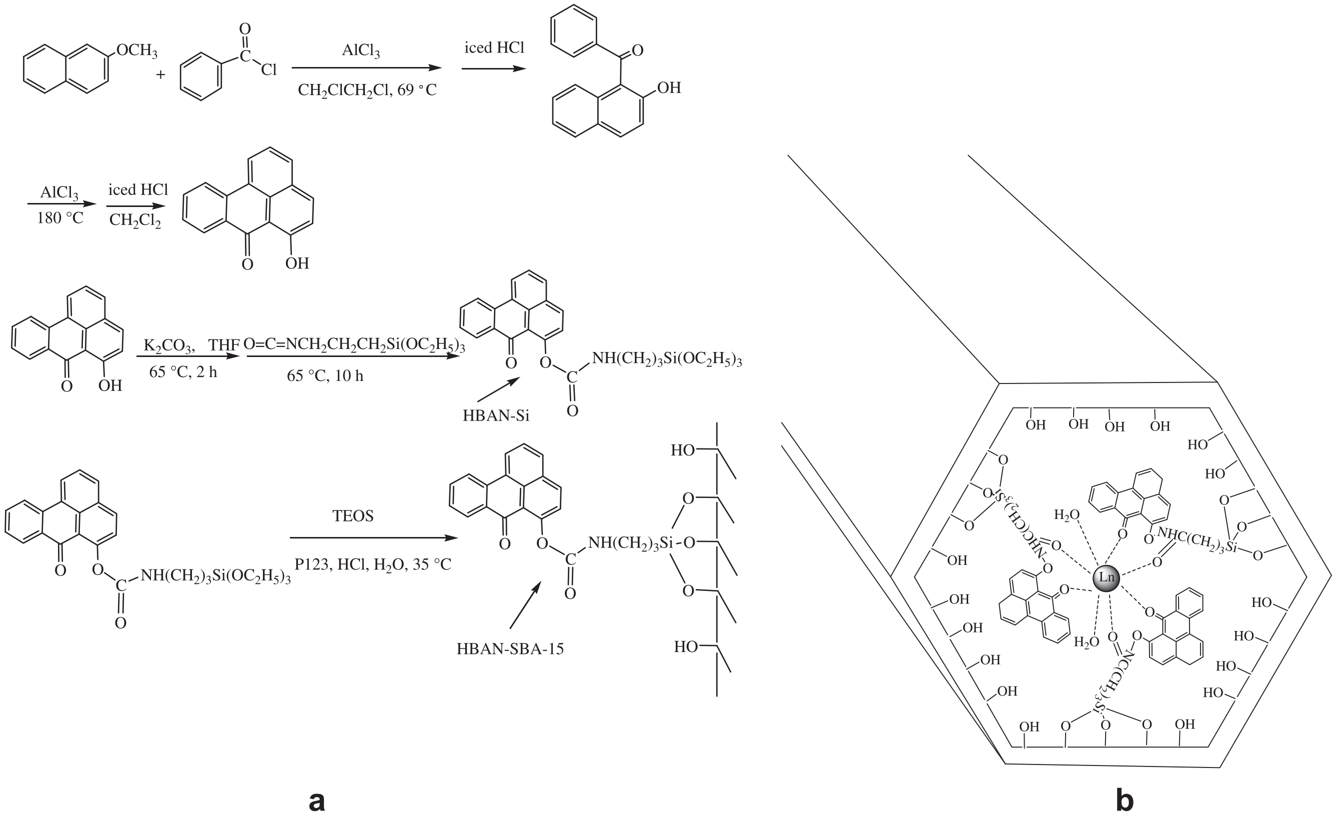

Fig. 1. Scheme of (a) synthesis of HBAN, HBAN-Si and HBAN-SBA-15; (b) predicted composition of $Ln(HBAN\text{-}SBA\text{-}15)_3(NO_3)_3$.