INTRODUCTION

Photo-luminescent lanthanide ions have received considerable attention in recent years because of their potential applications in the field of optoelectronics and cellular bioimaging. Efficient emission from lanthanide ions has been achieved by Resonance Energy Transfer (RET) phenomenon, where the excited state energy of a donor molecule is transferred to lanthanide ion through dipole-dipole interactions or electron-exchange process. It has been reported in the literature that ‘tunable’ emission and white light generation from lanthanide ions can be achieved by partial RET. The tunable emission from lanthanides have potential applications in the production of flat panel displays and portable display devices.

While RET can generate luminescent lanthanide ions efficiently, the emission from these ions can be easily deactivated in solution state by the high energy vibronic coupling promoted by the coordinated solvent molecules. In order to minimize the deactivation process during RET, lanthanide complexes can be incorporated in various matrices such as gels and micelles, where the solvent molecules can be replaced from the first coordination sphere of the lanthanide ion as a result of matrix interaction.

Anderson et al. have achieved tunable emission from lanthanide ions (Tb(III) and Eu(III)) in gel phase, where the gel was formed by the terpyridine appended PEG(poly ethylene glycol) polymer. In another attempt, Majiet et al. have generated white light emission utilizing lanthanide ions (Eu(III) and Tb(III)) in gel medium.

In the present study, we have investigated the RET process from various energy donors {NTCA, PDC, BDCA, and TA} to lanthanide ions (Eu(III), Tb(III)) in a clay based gel medium to achieve tunable emission. Aminoclay, an economically cost effective material, has been recently utilized as a scaffold to achieve multi-coloured and white light emission from organo-lanthanide gels.

Since carboxylate ions can coordinate well with the lanthanide metal ions to facilitate RET, we have investigated the energy transfer from 1,4,5,8-naphthalenetetra carboxylic acid (NTCA), 2,6-pyridinedicarboxylic acid (PDC), benzene-1,4-dicarboxylic acid (BDCA) and trimesic acid (TA)) to lanthanide ion acceptors (Tb(III) and Eu(III)).

ABSTRACT

The resonance energy transfer (RET) from various organic donors {1,4,5,8 naphthalenetetra carboxylic acid (NTCA), 2,6-pyridinedicarboxylic acid (PDC), benzene-1,4-dicarboxylic acid (BDCA) and trimesic acid (TA)} to lanthanide ion acceptors (Tb(III) and Eu(III)) has been analysed in an aminoclay based gel medium. The metal-centred emission quantum yield values indicate that the gel is a better medium to promote RET in the system, compared to solution state. The characterization study indicates that the organic donor molecules are electrostatically bound to the positively charged aminoclay surface, which regulates the distance between them to the lanthanide ion acceptor molecules. The metal-centred quantum yield values were 4.7% for NTCA-Eu(III), 2.5% for PDC-Eu(III), 2.6% for PDC-Tb(III), 1.9% for BDCA-Eu(III), and 1.4% for TA-Eu(III) in gel medium.

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Experimental Section

MATERIALS

Aminoclay (AC) was synthesized according to a previously reported procedure.\textsuperscript{21} 1,4,5,8- naphthalenetetracarboxylic dianhydride, 2,6-pyridinedicarboxylic acid, Trimesic acid and benzene-1,4-dicarboxylic acid were purchased from Sigma Aldrich, USA. All purchased materials were utilized without further purification, unless otherwise stated. Potassium salt of 1,4,5,8-naphthalenetetracarboxylic acid (NTCA), 2,6-pyridinedicarboxylic acid (PDC), Trimesic acid (TA) and benzene-1,4-dicarboxylic acid (BDCA) were obtained by dissolving all materials into aqueous solution of potassium hydroxide (0.1M). Europium/Eu(III) acetate and terbium/Tb(III) acetate were purchased from Central drug house, India. All experiments were performed in doubly distilled water.

Instrumentation: Mass spectra were recorded using a Micromass Q-TOF mass spectrometer. FT-IR spectra were recorded using JascoV-660 spectrophotometer at room temperature. The UV-vis absorption measurements were carried out using a Jasco V-660 spectrophotometer. Fluorescence experiments were recorded on a Horiba JobinYvon Fluoroma-4 fluorescence spectrophotometer. The X-Ray diffraction pattern (XRD) measurements were carried out by using Bruker D8 Advance X-ray diffractometer using Cu Ka radiation (\(\lambda = 1.54178 \text{Å}\)).

Synthesis of Aminoclay (AC) based Hydrogel

Lanthanide incorporated aminoclay based hydrogel was obtained by dissolving aminoclay (AC) (15 wt%) in adequate amount of doubly distilled water followed by the addition of potassium salt of any of the following energy donors {NTCA (0.015M), PDC (0.015M), TA (0.015M), BDCA (0.015M)}, based on our choice, along with the lanthanide (III) acetate (0.1M). The components were taken in a vial and sonicated for 4 minute, and the whole mass is converted into a gel phase. The hydrogel formation was confirmed by inverted vial method. The aminoclay based hydrogel was stable at room temperature.

Quantum yield calculation: Photoluminescence quantum yield of the gel samples were carried out by calibrated integrating sphere in a SPEX Fluorolog spectrophotometer. The sample keep in the sphere was excited using a Xe arc with 365 nm as the excitation wavelength. The absolute quantum yield was determined by de Mello method\textsuperscript{24} using the following equations.

$$\phi_{PL} = \left[\frac{E_i(\lambda) - (1 - A)E_o(\lambda)}{L_o(\lambda)A}\right]$$ ……. (1)

$$A = \left[\frac{L_o(\lambda) - L_i(\lambda)}{L_o(\lambda)}\right]$$ ……. (2)

Where \(E_i(\lambda)\) and \(E_o(\lambda)\) denote the integrated fluorescence intensity as a result of direct excitation and secondary excitation of the sample, respectively. \(A\) is the absorbance of sample, measured by using eq (2). \(L_o(\lambda), L_i(\lambda)\) and \(L_e(\lambda)\) represent the integrated excitation intensity for direct excitation, secondary excitation and excitation profile for an empty sphere, respectively.

Calculation of energy transfer efficiency (E): The efficiency of energy transfer was calculated by quantum yield measurement for metal-centered (Ln[III]) emission.\textsuperscript{25}

Calculation of rate of energy transfer (k): The rate of energy transfer (k) between donor and acceptor was quantified by the following equation.\textsuperscript{26}

$$k = \frac{E^{-1}}{1 - E}$$ ……. (3)

where \(\tau_D\) is the donor lifetime in the absence of acceptor and \(E\) represents the efficiency of energy transfer.

RESULTS AND DISCUSSION

Amino clay, which is a layered alumino-silicate talc like structure (2:1 trioctahedral), has high propensity to aggregate.\textsuperscript{27} Aminoclay was synthesized by utilizing magnesium chloride and 3-aminopropyltriethoxysilane. The X-ray diffraction pattern of aminoclay consists of a broad basal peak and three broad higher reflection pattern (Figure S1). Since aminoclay has talc-like phyllosilicate structure, the phyllosilicate has three higher angles in a plane reflection plane, which were d(020, 110) = 0.407 nm (2θ = 22°), d(130, 200) = 0.256 nm (2θ = 35°) and 2θ=59° (d=1.56 Å). Among all the reflection plane, the in plane reflection at 2θ=59° (d=1.56 Å) is a characteristic plane for the phyllosilicate.\textsuperscript{28}

The peripheral amino groups in the clay will be protonated in water and the protonated aminoclay self-assembles in presence of negatively charged organic sensitizers through electrostatic interaction.\textsuperscript{29} The aminoclay based hydrogel was prepared by mixing aminoclay along with organic sensitizers. The structure of the organic sensitizer is depicted in Chart 1.

![Chart 1](image)

**Chart 1.** Potassium salt of (I) 1,4,5,8-naphthalenetetracarboxylic acid (NTCA), (II) 2,6-pyridinedicarboxylic acid (PDC), (III) benzene-1,4-dicarboxylic acid (BDCA), and (IV) trimesic acid (TA).
Similarly, in the case of NTCA 234 nm due to complex formation with bands around 262 and 256 nm the absence of the metal ion, the absence and presence of the metal ion {Eu(III)}(0.1 M). In and trimesic acid (TA) [IV]{10 spectra of benzene photo

Figure 1 SEM images of xerogel of aminoclay consisted of (I)NTCA a absence and b) presence of metal ion {Eu(III)}(II) PDC) absence and d) presence of metal ion {Eu(III)}. The SEM images show identical morphologies which indicated that self-assembly was not interrupted by the metal ion.

Figure 2 shows the FT-IR spectra of the organoclay in the presence and absence of the metal ion {Eu(III)I. The carboxylate ion stretching frequency of organic sensitizer (PDC)\(^{38}\) was shifted from 1635 cm\(^{-1}\) to 1622 cm\(^{-1}\) after the encapsulation of metal ion {Eu(III}). Similarly, the carboxylate ion stretching frequency of NTCA, TA, and BDCA was also shifted after the addition of the metal ion {Eu(III)}(Figure S3). The FT-IR results indicate that the metal ion is coordinated to the organic sensitizers through the carboxylate anion.

Photo-physical study

Figure 3 (a) and (b) respectively represent the absorption spectra of benzene-1,4-dicarboxylic acid (BDCA) [III] {10\(^{-5}\)M} and trimesic acid (TA) [IV] {10\(^{-5}\)M} incorporated aminoclay, in the absence and presence of the metal ion {Eu(III)}(0.1M). In the absence of the metal ion, BDCA and TA show absorption bands around 262 and 256 nm,\(^{32}\) respectively, while in the presence of metal ion absorption bands were shifted to 250 and 234 nm due to complex formation with the metal ion {Eu(III)}. Similarly, in the case of NTCA and PDC in aminoclay, absorption bands were shifted after the incorporation of metal ion {Eu(III)} into the system. (Figure S4).

Figure 2. Normalized UV-vis absorption spectra of potassium salt of a) benzene-1,4-dicarboxylic acid (BDCA) (10\(^{-5}\)M) b) trimesic acid (TA) (10\(^{-5}\)M) incorporated aminoclay(15 wt%) in presence(red line) and absence (maroon line) of metal ion {Eu(III)} (0.1 M) (in gel state).

Figure 3. Normalized UV-vis absorption spectra of potassium salt of a) benzene-1,4-dicarboxylic acid (BDCA) (10\(^{-5}\)M) b) trimesic acid (TA) (10\(^{-5}\)M) incorporated aminoclay(15 wt%) in presence(red line) and absence (maroon line) of metal ion {Eu(III)} (0.1 M) (in gel state).

The results of photo-physical studies reveal that the organic sensitizers was interacted with lanthanide ion {Eu(III)}.

Initial results suggest that the self-assembly was promoted by the electrostatic interaction between the organic sensitizers and the aminoclay. Since the concentration of amino clay was much higher compared to that of the organic sensitizer, we presume that, the organic sensitizer acts as a cross linker between the amino clay units. While the presence of lanthanides is not essential for gelation, it is likely that lanthanides are sandwiched between the organic sensitizers, which connect the amino clay units. The results taken together suggest that lanthanide ion sandwiched between the organic sensitizers which is connected to the layered structure of aminoclay, as shown in the scheme 1.

Scheme 1. Schematic representation of the lanthanide ion and organic sensitizers in amino clay.

Furthermore, we have investigated resonance energy transfer from organic sensitizers to lanthanide ions {Eu(III) and Tb(III)} in the aminoclay based gel medium. Figure 4(a) represents the emission spectra of potassium salt of NTCA in gel phase (xerogel). After excitation the system at 340 nm, broad, structureless emission of naphthalene was observed at 438 nm which is assigned to the excimer formation, based on literature reports.\(^{33}\) Furthermore, after incorporation of the metal ion {Eu(III)} into the system, donor emission intensity was significantly quenched and subsequently metal-centered emission was enhanced due to resonance energy transfer. Figure 4 (b and c) shows the emission spectra of PDC in the presence of lanthanide ions {Tb(III) and Eu(III)}. The triplet state energy level of PDC and the resonance energy level of

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CONCLUSION

We have utilized the aminoclay based gel medium to investigate the efficient energy transfer from various donor molecules (NTCA, PDC, BDCA, TA) to acceptors {Eu(III) and Tb(III)}...The present study reveals that efficient energy transfer was observed in gel medium compared to solution phase.

Associated Content

FT-IR spectra of donor acceptors, Absorption spectra of different donor, Steady state luminescence spectra for different donor acceptor pair in solution phase.

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