

Micro-Meter Size Organogelator with Tri-Color Luminescence (Blue, Green and Red) Activated by Dy³⁺, Tb³⁺ and Eu³⁺ ions

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Abstract The preparation of a novel type of low-molecular-weight amphiphilic organogelator bearing three long 14-alkyl chains and hydrophilic oligo(oxyethylene) groups was described. Ultra-violet absorption and fluorescence spectra give evidence of the energy transfer between organic ligands to lanthanide ions. Characteristic green, blue and red luminescence of the organogels were obtained and interesting emission properties of terbium, dysprosium and europium ions were unexpectedly observed at the first time during the order-disorder phase transition point (29 °C).

Keywords Lanthanide · Luminescence · Organo-gels · Micro-meter

Introduction

Low-molecular-weight organo-gels (LMOGs) have drawn much attention in the past decade. Particularly, the smart gels can be tuned reversibly in external chemical, photochemical, thermal, sound, pH stimuli etc [1, 2]. The mechanism of the so-called self-assembly gelators is due to specific noncovalent intermolecular interactions such as van der Waal's forces, π - π stacking and hydrogen bonding interactions and the resulting gels are generally thermo-reversible [3–5]. Through increasing above the sol-gel

transition temperature, the gelator is fully dissolved and upon cooling to the room temperature, the suprastructure within the gels will be thus obtained.

On the other hand, with the development of modern coordination chemistry, various metal-sensitized organogels with elaborate structures have also been synthesized. It is rather appealing to find some correlation between the metal-gel structures and their corresponding optical properties [6]. Among diverse kinds of metal ions, lanthanide complexes exhibited well-defined luminescence that are typical by narrow emission lines, large Stokes shifts and long excited state lifetimes. Combined with soft matrices of LMOGs, they may show promising future in luminescence imaging and as sensors for special bioactive species. However, lanthanide ions have very low absorption coefficients and their corresponding emissions would be rather inefficient based on pure lanthanide salts. For the sake of harvesting more energy in the UV region, designed organic ligands with which the lanthanide ion is coordinate are considered to be compulsory [7]. In this case, the lanthanide gives its characteristic emission with high efficiency via the energy transfer process from the ligands as antennas. In fact, the forbidden intraconfiguration f-f transitions of lanthanide ions are easily recognizable and stable regardless of different ligand-field split bands, their emission colors cover the entire spectrum from ultra-violet to visible and near-infrared region (0.3–2.2 μ m), making them ideal candidates for optical probes and preparing trichromatic devices for potential lighting purposes. Hence, it is very interesting to study their attractive photophysical properties in the entire visible range when they were trapped inside gels. Presently, a few researches were concentrated on noncovalent incorporation of lanthanide ions into polymeric gels [8]. But very limited studies focused on lanthanide functional LMOGs as far as we

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know [9, 10]. Actually, molecular gels have more precise and simple structure, can be easy to identify and possibly possess particular coordination abilities with lanthanide ions on the molecular scale.

In terms of sensitizing organic ligands, we found that aromatic carboxylic acids have emerged as the suitable ligands for terbium and dysprosium ions because of energy match between their triplet state levels and resonant energy levels of central rare earth ions [11, 12]. As a result, we designed and synthesized a novel organogelator based on aromatic ring named as ligand 1 (Fig. 1). Previously, we synthesized a class of similar aromatic compounds with triethoxysilane terminals [10]. But the above derivatives decreased their solubilities in common organic solvents and the respective organo-gels easily collapsed or precipitated from matrices. To circumvent this problem, more hydrophilic moieties such as oxyethylene were introduced into the gel structure. The final synthesized ligand 1 can be dissolved in CHCl_3 , CH_2Cl_2 or THF completely and molecular structure was confirmed by $^1\text{H-NMR}$ and TOF-Mass spectra (see supplementary section). White gels were formed in EtOH and MeOH (Scheme 1). The take place of triethoxysilane groups dramatically reduced the gel to sol transition temperature as low as 29 °C. All the tested gels remained to be physically stable after the treatment of heat and cool cycles for more than ten times.

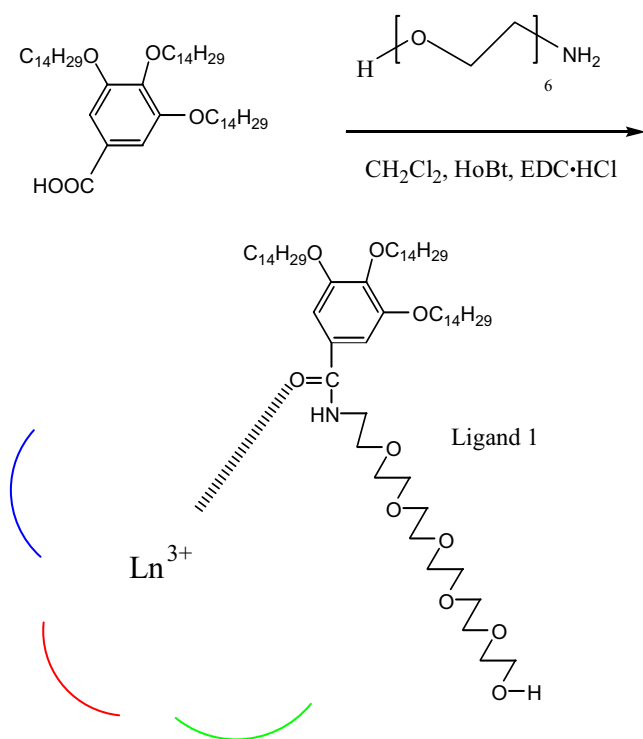


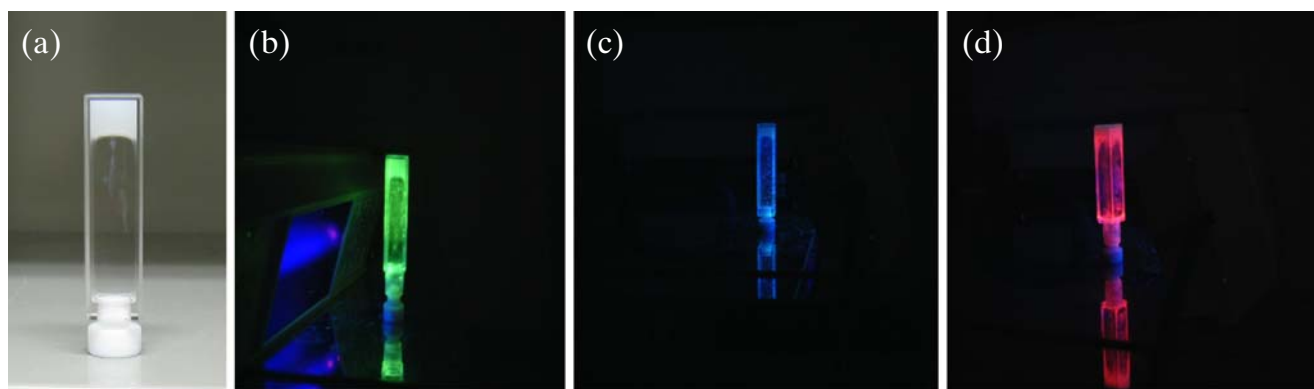
Fig. 1 Molecular structure of ligand 1

Results and discussions

Although ligand 1 does not contain carboxylate group, in contrast to the uncharged oxygen atoms such as ether or ethanol, the partially negatively charged oxygen atom in amide group could form relatively stable coordination bonds and transfer the harvested energy to central lanthanide ions which we can find concrete evidence in a few published results [13]. We have to admit that the doped lanthanide ions should have some influence on the gelation property because the low critical gelation concentration for pure organogel is 30 mg/ml in ethanol, whereas terbium, dysprosium and europium gels are 34 mg/ml, 46 mg/ml, 46 mg/ml respectively.

In the very beginning, the UV region activity and photoluminescence properties of ligand 1 were performed. Figure 2 presents the absorption spectra and the excitation bands of ligand 1, the superimposition of the two bands show that the $\pi\text{-}\pi^*$ transition of the benzene ring of ligand 1 is accountable for the singlet excited state within the molecule. Further study provides the emission peak of ligand 1 and the excitation band of terbium or dysprosium containing organogel, according to the energy migration mechanism [14], the large overlap between the above three lines predicts the possible efficient energy transfer from the donor (ligand 1) and acceptor (Tb^{3+} and Dy^{3+}) (Fig. 3). As a consequence, we successfully prepared Tb and Dy activated organogels by simply introducing terbium and dysprosium salts which are regarded as nearly inert under UV light. Strong green and blue luminescence were clearly observed at the UV 254 excitation in the gel state (Scheme 1). Though ligand 1 with fluorescence peak wavelength at 341 nm is thought to be slightly higher and not suitable for sensitizing Eu^{3+} based on Forst-Dexter resonant exchange interaction and thermal de-activation mechanism [15], it is still appealing to fabricate gels with intense red luminescence originated from $\text{NH}_4(\text{Eu}(\text{TTA})_4)$ (TTA = thenoyltrifluoroacetate) complexes and ligand 1. Unexpectedly, the three Tb, Dy and Eu metal gels behave completely different under temperature-responsive sol-gel transition stage and engender rather interesting luminescence variation phenomenon.

The excitation spectra of Tb gels shown in Fig. 4 starting at room temperature exhibit the center of the peak wavelength is around 335 nm which is overlap with fluorescence band of ligand 1 at 341 nm (Fig. 3) but displays 6 nm blue shift ascribed to terbium coordination with amide groups of ligand 1 (Tb-O bonds). With regard to coordination, it can be observed that the dotted line in Fig. 4 is the excitation spectra of terbium ions solely in ethanol and its peak locates at 275 nm, the 50 nm red shifts in the baricenter by the excitation peak of terbium gel relative to the pure terbium ions are caused by the



Scheme 1 Pure gel under Room light (a) and Terbium (b), Dysprosium (c) and Europium(d) containing gels excited at UV light $\lambda_{\text{ex}}=254$ nm

nephelauxetic effect and suggest the existence of coordination interactions and the site isolation of terbium ions by this chemical bond [16]. Along with the temperature increase from 20 °C to 45 °C, the changes of excitation line can be clearly observed as gradual decrease of its emission intensities, indicating that Tb-O interactions has been weakened attributed to higher temperature. Because the emissive energy level of ligand 1 is closely matched with the resonant energy level of terbium ions (Fig. 3), its complex yields very strong green fluorescence of terbium within our expectation. Due to the intense emission of the gel, we restricted excitation and emission slits as only 2.5 nm, still the four characteristic intra-configuration f-f transition of terbium ions from 5D_4 excited states to the different J levels of the ground term 7F_J ($J=6, 5, 4, 3$) were clearly seen. The dominant band of $^5D_4 \rightarrow ^7F_5$ located at 546 nm is very sharp, showing an excellent color quality of the transition. Concerning the temperature dependence issue, it corresponds to excitation spectra exactly. The peak intensity in the gel state (20 °C) continued to reduce from 1,623 to 1,080 at 45 °C (Fig. 5). Lately, Carlos L.D. et al [17] reported a photoluminescent hierarchically structured bilayer alkylene/siloxane called monoamidasil which has

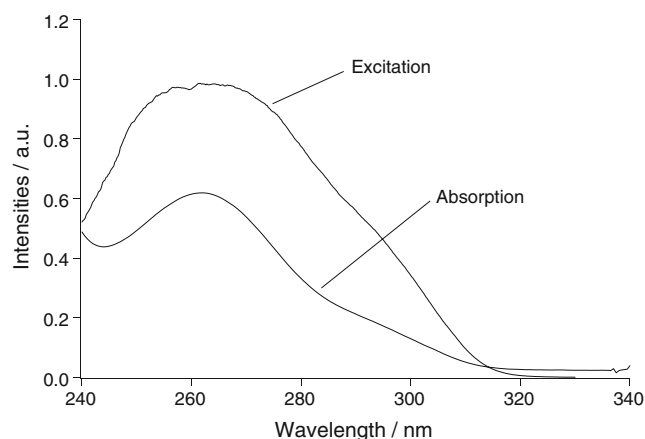
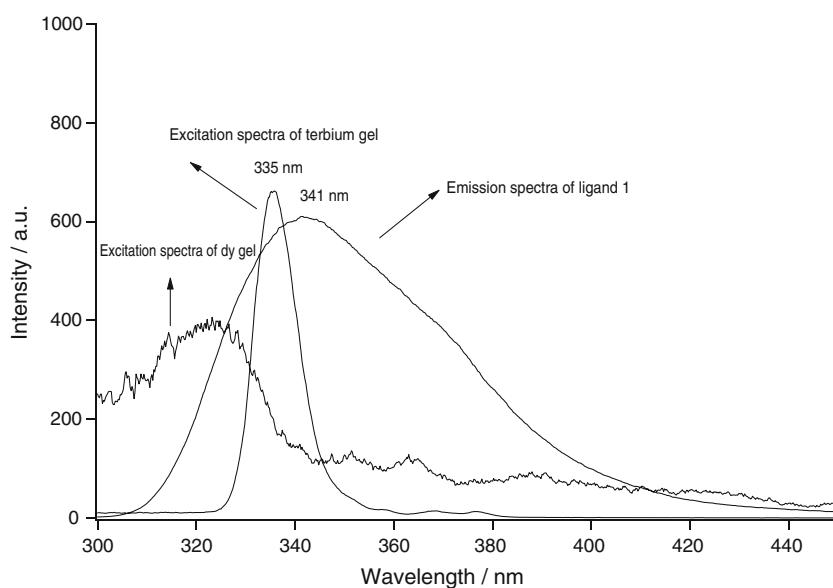


Fig. 2 Absorption spectra of ligand 1 (1×10^{-5} M) in ethanol and its excitation spectra with $\lambda_{\text{em}}=341$ nm

some similarity to our ligand 1 with the major difference that monoamidasil lacks aromatic ring. In their study, the heating-cooling cycle operating between room temperature to higher degree triggers the order-disorder phase transition due to the presence of hydrophobic interactions between the organic chains. Accordingly, the proposed mechanism of the emission change is as follows: at room temperature (20 °C), the gel state is quite stable and the long alkyl chains could surround the coordinated terbium ions in a highly ordered manner and protect them from attacking by ethanol which may quench the luminescence easily through $-\text{OH}$ vibrations, while the gel reaches at the middle of gel and sol (25–30 °C), ethanol could participate into coordination site of terbium, thus the luminescence has decreased. After the gel completely turns into solution (31 °C), the aliphatic chains become less stretched and more loosely packed, the van der Waal's forces were therefore disrupted and induced the aggregation of terbium ions. In addition, the high temperature speed up the non-radiative deactivation process, therefore, the fluorescence intensities of terbium lost more than 30% of its origin.

In a bit different manner, the Dy containing metal gel shows another unique way of temperature dependence luminescence changes (Fig. S1). In the gel state and up to until 30 °C, the peak intensities of excitation spectra slowly decreased and red shifts from 319 nm to 325 nm, giving evidence that Dy-O coordination exists inside the organogels. Whereas above the T_{gel} , the relative intensity of the spectra has increased more than two fold at 35 °C and the center of the band has a surprising bathochromic shift from 325 nm to 335 nm which is definitely contrary to the previous terbium gel. In regard to this enhanced and broad band covering from 320 nm to 400 nm range, we initially deduced that it was attributed by the organogel itself and its dissociation with Dy^{3+} ions. With direct excitation ($\lambda_{\text{ex}}=320$ nm) of the ligand, we obtained the emission spectra (Fig. 6), two sharp peaks located at blue (480 nm) and yellow region (573 nm) were easily identified and they corresponded to $^4F_{9/2} \rightarrow ^6H_{15/2, 13/2}$ transitions of dyspro-

Fig. 3 Excitation spectra of terbium and dysprosium gels and emission spectra of ligand 1 with $\lambda_{\text{ex}}=262$ nm



sium ions respectively at room temperature. Compared with terbium system, the intensity of emission spectra of Dy gel has reduced enormously even when we selected excitation and emission slits as 5 nm, demonstrating that the intramolecular energy transfer from ligand 1 to Dy^{3+} is less favorable than Tb^{3+} . Interestingly, when the temperature increased to 30 °C, the emission bands have gone down stepwise as evidenced by the above excitation spectra. But when it was heated above 32 °C, it is rather interesting to obtain one broad band located between 360 nm to 600 nm, covering a large part of the visible spectrum area (Fig. 6). In contrast to the previous results [10], the emission from Dy^{3+} still remained and luminescence was not switched off. It is estimated that ligand 1 binds with Dy more effectively than triethoxysilane group bearing compound as we

reported before. According to the publication concerning white phosphors lacking metal ions [18] and the urethane hybrid materials [19], it is estimated that this strong emission is related to lone pair of electrons of the NH-group in ligand 1 and probably photo-induced proton-transfer between defects such as NH_2^+ and N^- occurs. However, this typical band for ligand 1 hardly appears in terbium gel, showing that the energy match between the ligand and terbium gains more advantage than dysprosium and the intensity of blue band is almost invisible and quenched in terbium system, so the green luminescence is the prominent one under the UV light excitation.

Since the triplet level of the β -diketonate is at 490 nm ($20,400 \text{ cm}^{-1}$) [20] which would be excellent sensitizing ligands for europium ions, we firstly prepared $\text{NH}_4(\text{Eu}$

Fig. 4 Temperature dependence of excitation spectra of terbium containing gel with $\lambda_{\text{em}}=545$ nm and excitation of $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ in ethanol (10^{-4} M)

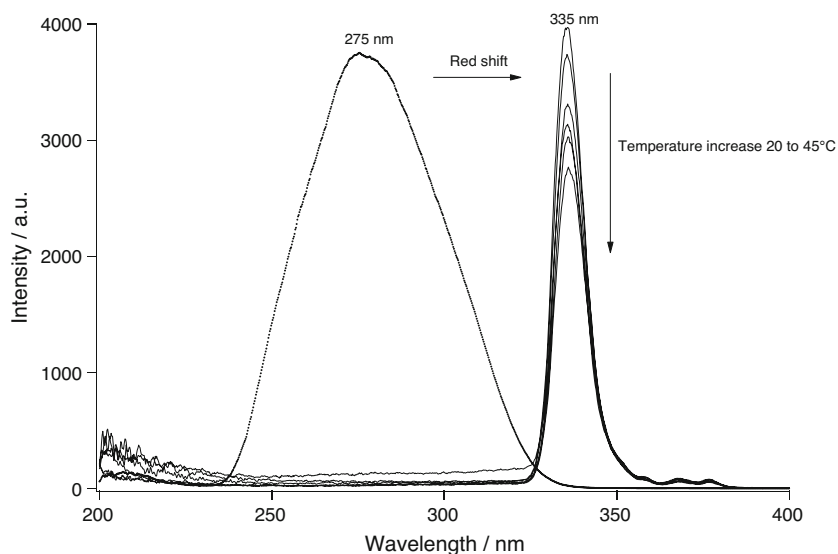
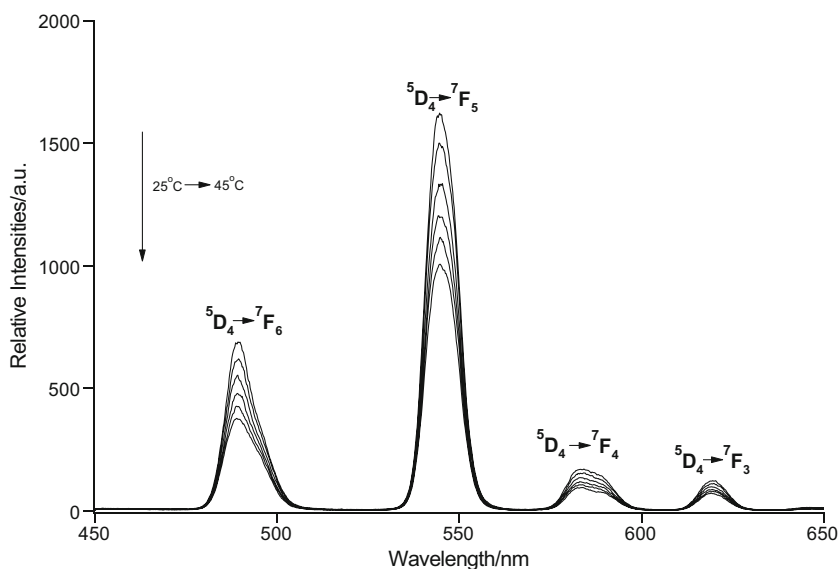


Fig. 5 Temperature dependence of emission spectra of terbium containing gel with $\lambda_{\text{ex}}=335$ nm



(TTA)₄) complex crystals through previous reference [21], then introduced the binary complex into ligand 1 as matrices. The excitation spectra of europium complex containing gel were monitored at 613 nm (Fig. S2). Almost no f-f transitions could be noticed because they are very weak (small peaks at around 470 nm may be attributed to europium f-f transitions). The observed broad bands from 20–25 °C in the range of 300–400 nm prove that ligand 1 absorbs light in this region that is similar to dysprosium case. Upon the temperature increase, the large band also gradually changes and peak intensity has decreased. At 30–35 °C, the band begins to be separated and a new peak at around 390 nm can be clearly detected. After the gel transforms into solution completely at 35 °C, the excitation spectra undergoes a tremendous change that the predomi-

nant peak wavelength becomes to be 390 nm that is the characteristic excited transition of β -diketonate ligand [22], suggesting that the coordination interactions between europium β -diketonate complex and ligand 1 are destroyed and only TTA acts as a primary role in excitation although a weak and flat band still can be observed in the 300–400 nm region. As expected, we can obtain desired red emissions of europium ions and the narrow peaks detected in the luminescence spectra are transitions from 5D_0 excited states to different J levels of the ground term 7F (7F_J , $J=0,1,2,3,4$). The $^5D_0 \rightarrow ^7F_2$ transition (613 nm) is the dominant peak and contributes to the red emission (Fig. 7). From 20 °C to 30 °C, the luminescence intensity has been gradually increased from 804 to 1,374 in the gel state. But after the coordination bond between europium complex and

Fig. 6 Temperature dependence of emission spectra of dysprosium containing gel with $\lambda_{\text{ex}}=320$ nm for 20–30 °C, 335 nm for 35 °C

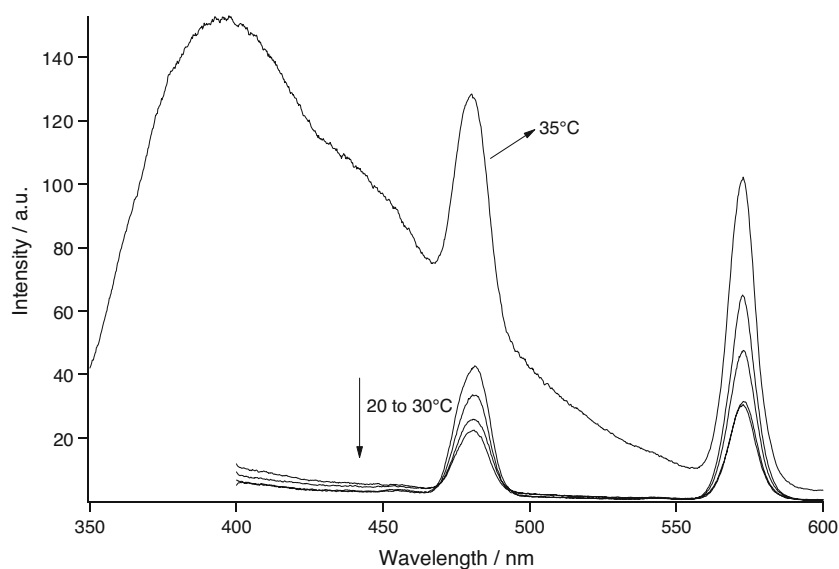
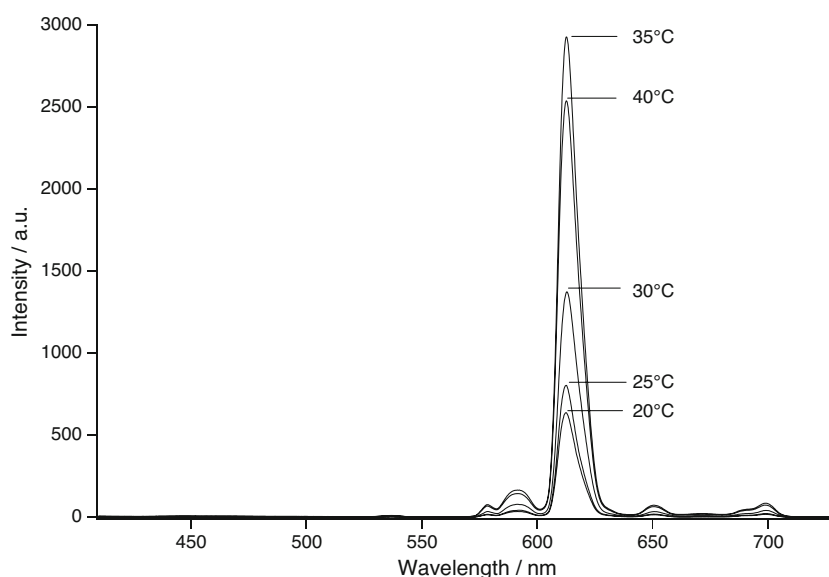


Fig. 7 Temperature dependence of emission spectra of europium containing gel with $\lambda_{\text{ex}}=320$ (20–30 °C) or 391 nm (more than 35 °C)



-C=O groups of ligand 1 disrupted, the released free complex exhibits very distinguished europium emission signal and its intensity is nearly four times (2,927 at 35 °C versus 804 at 20 °C) higher than in the gel stage under the excitation wavelength at 391 nm even we modified the excitation and emission slits as 2.5 nm (20 °C is 5 nm). In this way, we can make the red luminescence tunable (from current level to much enhanced signal) by ordinary temperature variation which might serve as candidates for optical signal amplifiers and biological markers or assays.

The overall quantum yields and luminescence lifetimes (τ) were both investigated for the three organo-gels (Table 1). The measured decay curves of all the samples belong to monoexponential kinetics, which indicate that only one coordination species existed in the soft matrices. In terms of the above results, we can conclude that ligand 1 prefers terbium ions for more effective energy migration compared with dysprosium ions that is also found in photoluminescence studies.

Size measurement

Dynamic light scattering was used to characterize the aggregated gels upon temperature dependence (Fig. S3). At room temperature, the intermolecular self-assembly takes place and aggregates clearly formed with the average

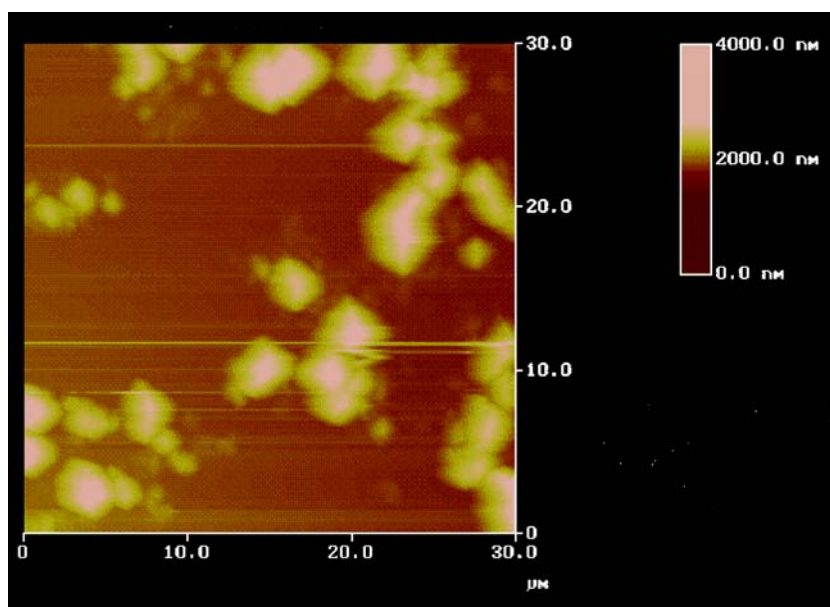
Table 1 Overall quantum yields and lifetimes of three gels

	Excitation/nm	Φ_{overall}	$\tau/\mu\text{s}$
Tb-gel	335	3.7%	368
Dy-gel	320	0.8%	93
Eu-gel	320	6.2%	410

diameter size around 5 μm . The experimental records display a general tendency of decreasing diameter as the temperature enhanced. After heating across T_g , the gel size has reduced to 2 μm probably due to release of large amount of solvent molecules. A further examination of AFM results also clarified the range of the organo-gel diameter size distribution (Fig. 8). We can observe the terbium gel was composed of micrometer-sized particles with the length and diameter 4–5 μm which are consistent with DLS measurement. The thickness of the soft granule might be 600–700 nm based on the data analysis (Fig. S4). We choose terbium gel as an example, Dy and Eu sensitized gels both exhibited similar DLS or AFM results (Figs not shown).

Conclusions

A novel low-molecular-weight amphiphilic organogelator which bears amide group (-CONH-) was synthesized. Optical centers Tb^{3+} , Dy^{3+} and Eu- β -diketonate complex have been introduced into the soft host and generated tri-color (green, blue and red) photoluminescence properties due to the coordination with amide moieties of ligand 1 (Tb and Dy). In brief, i) we found stepwise reduction of green emission from terbium gel during the gel-to-sol transition point due to the firm coordination capability of terbium ions; ii) complexation collapse between ligand 1 and Dy^{3+} in sol state and a broad blue band has been identified which is promising in the design of white light device; iii) interaction disruption between europium complex and ligand 1 was noticed and four times of red emission enhancement was clearly observed during this phase change which is sharply in contrast to the luminescence decrease of terbium gel.

Fig. 8 AFM image of terbium gel

Experimental

All materials were obtained from commercial suppliers and used as received. DMF was distilled under reduced pressure and other solvents were used as provided. N_2 was used after drying by $CaCl_2$. All reactions were monitored by TLC and separated by Merck silica gel with 230–400 mesh. 1H -NMR spectra were recorded at 293K on Bruker DRX 400 (400 MHz). Fluorescence spectra were measured on Edinburgh FLS920 spectrometer, the excitation and emission slits for Tb activated gel (2.5,2.5 nm), for Dy (5.0,5.0 nm) and for Eu (2.5–5.0 nm) respectively. Ultraviolet absorption was measured on Shimadzu 3,000 equipment. Fluorescence lifetimes were recorded in Edinburgh FLS920 with microsecond pulse lamp excitation. TOF-MASS spectra were measured with a Shimadzu spectrometer. Quantum yields were measured in integration sphere with Hamamatsu photonics absolute PL quantum yield measurement system C9920-02. For AFM observations, the gel samples were dispersed by minimal amount of chloroform and drying on mica at RT. The images were obtained in tapping mode by using a Nanoscope Veeco instrument. The elemental analyses were performed with Vario EL III analyzer system.

The preparation of 3,4,5-tris(tetradecoxy)benzoic acid and 3,6,9,12,18-hexaoxa-octadecyl amine have been reported in previous references [10, 23].

Synthesis of ligand 1: 3,4,5-tris(tetradecoxy)benzoic acid (0.14 g, 0.2 mmol) was fully dissolved in CH_2Cl_2 (10 ml) and 1-hydrobenzotriazole (HOBt) (0.2 mmol, 0.034 g), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC·HCl) (0.2 mmol, 0.046 g) were also added into the

mixture. 3,6,9,12,18-hexaoxa-octadecyl amine (0.4 mmol) was then dropped into the solution slowly. After 2 h, the reaction was almost finished by TLC monitor. 4% $NaHCO_3$, NaCl were used to purify the mixture and dried over Na_2SO_4 then concentrated in vacuo. Silica gel with $CHCl_3$ /methanol=100/1 gave 1 (0.12 g, 60% yield). 1H -NMR ($CDCl_3$) δ =7.04 (2H, s, 2,6-H), 4.01 (2H, t, J =6.4 Hz, 4-OCH₂), 3.98 (4H, t, J =6.0 Hz, 3,5-OCH₂), 3.66–3.50 (24H, m, $CH_2OCH_2 \times 6$), 1.82 (6H, m, 3,4,5-OCCH₂), 1.46 (6H, m, 3,4,5-OC₂CH₂), 1.25 (60H, m, 3,4,5-OC₃C₁₀H₂₀), 0.88 (9H, t, J =6.6 Hz, 3,4,5-OC₁₃CH₃). MS (TOF) found m/z 1,044 ($M + Na^+$), 1,060 ($M + K^+$), calcd for $C_{61}H_{115}NO_{10}$, 1,021. EA found: C, 71.62; H, 11.39; N, 1.39%, Anal. Calcd for $C_{61}H_{115}NO_{10}$: C, 71.65; H, 11.34; N, 1.37%.

Preparation of $NH_4(Eu(TTA)_4)$ complex: 4 mmol thenoyltrifluoroacetate was dissolved in boiling ethanol and 4 mmol ammonium was added. The mixture was heated to boiling and 1 mmol $Eu(CH_3COO^-)_3 \cdot 4H_2O$ in ethanol was added, filter the hot solution and 2 days later, orange-red like crystals were grown from the filtrate.

Preparation of luminescent gels: 0.64 mg $TbCl_3 \cdot 6H_2O$ was added into 0.5 ml ethanol and 17 mg ligand 1 was also put into the solution. Slowly heated to 65 °C and the solution turns into clear. The solution was cooled down to room temperature and after overnight, the gel was formed. 1 mg $Dy(NO_3)_3 \cdot 5H_2O$ was treated with 23 mg ligand 1 in the same manner and gel was prepared. 1 mg $NH_4(Eu(TTA)_4)$ was mixed with 23 mg ligand 1 and gel forms in the similar case. All gels are relatively stable and can stand in the room temperature for more than 1 month. All the tests for the gelation properties in ethanol were conducted by stable-to-inversion of the test tube method [24].

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References

- George M, Weiss RG (2006) Molecular organogels. Soft matter comprised of low-molecular-mass organic gelators and organic liquids. *Acc Chem Res* 39:489–497. doi:10.1021/ar0500923
- Nakashima T, Kimizuka N (2002) Light-harvesting supramolecular hydrogels assembled from short-legged cationic L-glutamate derivatives and anionic fluorophores. *Adv Mater* 14:1113–1116. doi:10.1002/1521-4095(20020816)14:16<1113::AID-ADMA1113>3.0.CO;2-U
- Cicchi S, Ghini G, Lascialfari L, Brandi A, Betti F, Berti D, Ferrati S, Baglioni P (2007) A new organogelator based on an enantiopure C₂ symmetric pyrrolidine. *Chem Commun* 1424–1426
- Camerel F, Bonardi L, Schmutz M, Ziessel R (2006) Highly luminescent gels and mesogens based on elaborated borondipyrromethenes. *J Am Chem Soc* 128:4548–4549. doi:10.1021/ja0606069
- Zhou YF, Xu M, Yi T, Xiao SZ, Zhou ZG, Li FY, Huang CH (2007) Morphology-tunable and photoresponsive properties in a self-assembled two-component gel system. *Langmuir* 23:202–208. doi:10.1021/la061530x
- Weng W, Benjamin Beck J, Jamieson AM, Rowan SJ (2006) Understanding the mechanism of gelation and stimuli-responsive nature of a class of metallo-supramolecular gels. *J Am Chem Soc* 128:11663–11672. doi:10.1021/ja063408q
- Bunzli JCG (2006) Benefiting from the unique properties of lanthanide ions. *Acc Chem Res* 39:53–61. doi:10.1021/ar0400894
- McCoy CP, Stomeo F, Plush SE, Gunnlaugsson T (2006) Soft matter pH sensing: from luminescent lanthanide pH switches in solution to sensing in hydrogels. *Chem Mater* 18:4336–4343. doi:10.1021/cm060603v
- Benjamin Beck J, Rowan SJ (2003) Multistimuli, multiresponsive metallo-supramolecular polymers. *J Am Chem Soc* 125:13922–13923. doi:10.1021/ja038521k
- Wang QM, Ogawa K, Toma K, Tamiaki H (2008) A novel luminescent organogel containing dysprosium ions quenched by gel-to-sol transition. *Chem Lett* 37:430–431. doi:10.1246/cl.2008.430
- Wang QM, Yan B (2004) Novel luminescent terbium molecular-based hybrids with modified meta-aminobenzoic acid covalently bonded with silica. *J Mater Chem* 14:2450–2454. doi:10.1039/b402667e
- Wang QM, Yan B (2006) Designing a family of luminescent hybrid materials by 3-(triethoxysilyl)-propyl isocyanate grafted 2-hydroxynicotinic acid bridge molecules. *J Organomet Chem* 691:3567–3573. doi:10.1016/j.jorganchem.2005.12.061
- Carlos LD, Sa Ferreira RA, Goncalves MC, De Zea Bermudez V (2004) Local coordination of Eu(III) in organic/inorganic amine functionalized hybrids. *J Alloy Comp* 374:50–55. doi:10.1016/j.jallcom.2003.11.063
- Li HR, Lin J, Zhang HJ, Fu LS, Meng QG, Wang SB (2002) Preparation and luminescence properties of hybrid materials containing europium(III) complexes covalently bonded to a silica matrix. *Chem Mater* 14:3651–3655. doi:10.1021/cm0116830
- Sato S, Wada M (1970) Relations between intramolecular energy transfer efficiencies and triplet state energies in rare earth β-diketone chelates. *Bull Chem Soc Jpn* 43:1955–1962. doi:10.1246/bcsj.43.1955
- Judd BR (1962) Optical absorption intensities of rare earth ions. *Phys Rev* 127:750–760. doi:10.1103/PhysRev.127.750
- Carlos LD, De Zea Bermudez V, Amaral VS, Nunes SC, Silva NJO, Sa Ferreira RA, Rocha J, Santilli CV, Ostrovskii D (2007) Nanoscopic photoluminescence memory as a fingerprint of complexity in self-assembled alkyl/siloxane hybrids. *Adv Mater* 19:341–344. doi:10.1002/adma.200601435
- Green WH, Le KP, Grey J, Au TT, Sailor MJ (1997) White phosphors from a silicate-carboxylate sol-gel precursor that lack metal activator ions. *Science* 276:1826–1828. doi:10.1126/science.276.5320.1826
- Carlos LD, Sa Ferreira RA, Pereira RN, Assuncao M, De Zea Bermudez V (2004) White-light emission of amine-functionalized organic/inorganic hybrids: emitting centers and recombination mechanisms. *J Phys Chem B* 108:14924–14932. doi:10.1021/jp049052r
- Binnemans K (2005) Handbook on the physics and chemistry of rare earths, Elsevier B. V. chapter 225:107–113
- Melby LR, Rose NJ, Abramson E, Caris JC (1964) Synthesis and fluorescence of some trivalent lanthanide complexes. *J Am Chem Soc* 86:5117–5125. doi:10.1021/ja01077a015
- Puntus LN, Schenk KJ, Bunzli JCG (2005) Intense near-infrared luminescence of a mesomorphic ionic liquid doped with lanthanide beta-diketonate ternary complexes. *Eur J Inorg Chem* 23:4739–4744. doi:10.1002/ejic.200500593
- Yoshitomi T, Yabuki S, Kawakami H, Sato R, Toma K, Furuhashi M, Maitani Y (2006) The structure of artificial lipids possessing oligo(ethylene glycol) and their behavior in water. *Colloids Surf A Physicochem Eng Asp* 284–285:276–283. doi:10.1016/j.colsurfa.2006.02.057
- Tam AYY, Wong KMC, Wang GX, Yam VWW (2007) Luminescent metallo-gels of platinum(II) terpyridyl complexes: interplay of metal center dot center dot center dot metal, pi-pi and hydrophobic-hydrophobic interactions on gel formation. *Chem Commun (Camb)* 2028–2030. doi:10.1039/b705062c