# Effective and efficient photoluminescence of salicylate-ligating terbium(III) clusters stabilized by multiple phenyl–phenyl interactions†

**Kazuhiro Manseki and Shozo Yanagida***

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**A luminescent nonanuclear terbium(III) hydroxo cluster, $Tb_9(Hesa)_{16}(\mu\text{-}OH)_{10}(NO_3)$ (Hesa: hexyl salicylate), stabilized by unique two-way phenyl ring interactions, π-π stackings ($d$ = 3.482–3.599 Å) and C–H-π interactions ($d$ = 2.75–3.03 Å) between adjacent pairs of salicylates, was structurally characterized based on X-ray analysis, and the favourable absorption change and efficient photoluminescent characteristic were rationalized as being due to *J*-type π-π stackings, which are dramatically enhanced by hexyl groups in hexyl salicylate ligands.**

In parallel to the recent advancement of violet LEDs, there is an increasing interest in the development of luminescent compounds capable of converting the near-UV light (*e.g.*, 360–400 nm) to strong visible emissions. Lanthanide(III) coordination compounds exhibiting characteristic narrow emission bands, due to the intra-4f transitions, have been regarded as one of the key luminophores in fabricating light-emitting devices.[1] They can also be used in probes to recognize biologically important molecules.[2]

A large number of lanthanide(III) complexes with organic 'antenna chromophores', such as benzophenone and pyridine derivatives having high molar absorption coefficients ($\varepsilon$), have been developed for enhancing lanthanide(III) luminescence by UV light excitation around 300–360 nm.[3] In principle, irradiation of UV light to such lanthanide(III) chelates gives efficient energy transfer from the ligand π-π* state to the excitation level of emitting lanthanide(III) ions. This is followed by remarkable photosensitized luminescence. Consequently, these studies also give us criteria for molecular designs, *e.g.*, the need to suppress vibrational excitation due to coordinating water and solvent molecules, and allow us to rigidify the lanthanide coordination geometry.[4] However, few studies have been reported on lanthanide(III) complexes which enable longer wavelength sensitization of lanthanide(III) luminescence.[5]

We have recently found that polymetallic Eu(III) complexes with 2-octyloxy-4-hydroxybenzophenone or 2-dodecyloxy-4-hydroxybenzophenone have the great advantage of realizing strong red emission by near-UV, or even blue light, illumination.[6] However, their detailed structural analyses, which would allow us to fully understand the luminescent property, were unsuccessful. We anticipated that multiple phenyl–phenyl contacts of ligands (*e.g.*, non-covalent π-π stackings induced by hydrophobic assemblies of alkylated photosensitizing ligands around an inorganic cluster periphery) could make rigid inorganic–organic chelates. As a consequence, such cluster compounds could have the following merits: (i) red-shift of the absorption band due to phenyl stackings; and (ii) increasing $\varepsilon$ value coming from relatively large number of aromatic ligands which contribute to the effective luminescence at longer wavelength.

We will focus here on the Tb(III) hydroxo clusters exhibiting green photoluminescence. We have recently found that salicyl esters are suitable photosensitizing ligands for enhancing Tb(III) luminescence.[7] By using salicyl esters, two nonanuclear Tb(III) clusters, $Tb_9(Hesa)_{16}(\mu\text{-}OH)_{10}(NO_3)$ (TNS-He) with hexyl salicylate (H-Hesa) and the analogous compound $Tb_9(Mesa)_{16}(\mu\text{-}OH)_{10}(NO_3)$ (TNS-Me) of methyl salicylate (H-Mesa) were synthesized‡, and their luminescent features were rationalized to provide a novel method of tailoring Tb(III) luminophores for near-UV light excitation.

A single crystal of TNS-He suitable for X-ray structural analysis was successfully obtained by slow evaporation of the reaction mixture in methanol§. Fig. 1 shows the crystal structure of $[Tb_9(Hesa)_{16}(\mu\text{-}OH)_{10}]^+$. The compound is comprised of an 'inorganic' nonanuclear Tb(III) cluster bridged by hydroxo ions in which two square planes of $Tb_4(Hesa)_8(\mu_4\text{-}OH)$ (top and bottom parts of the cluster illustrated in Fig. 1, Tb–Tb distance 3.602–3.621 Å) are twisted at 45° to each other around the central Tb(III) ion, making two square pyramidal units through $\mu_3$-OH bridges. The central Tb(III) ion lies on a two-fold axis in the crystal structure. There are two different coordination sites with respect to

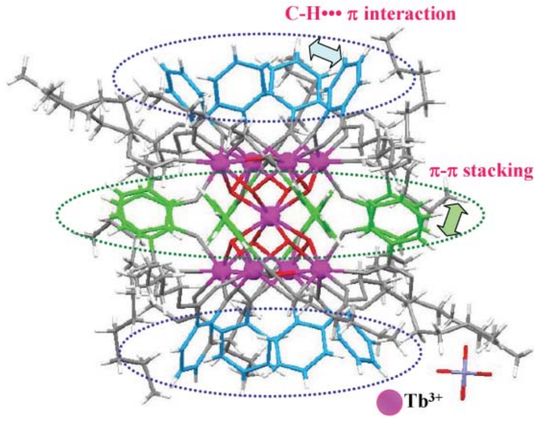

**Fig. 1** Crystal structure of TNS-He. Nitrate ion is disordered. Non-covalent phenyl contacts are also represented. ($Tb^{3+}$ pink, $\mu$-OH bridges red).

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*Center for Advanced Science and Innovation, Osaka University, 2-1, Yamada-oka, Suita, Osaka 565-0871, Japan. E-mail: k-manseki@casi.osaka-u.ac.jp; yanagida@mls.eng.osaka-u.ac.jp;*
*Fax: +81-6-6879-7351; Tel: +81-6-6879-7351*

† Electronic supplementary information (ESI) available: crystal data for $C_{208}H_{282}N_{61}Tb_9$. See DOI: 10.1039/b616387d

Tb(III) ions ($\text{Tb}_{\text{outer}}$–$\text{Tb}_{\text{center}}$ distance, 3.663–3.700 Å). Roesky *et al.* have pointed out that such cluster compounds including square pyramidal units are a common structural motif for lanthanide(III) clusters.[8] As for ligands of TNS-He, there are two unequivalent hexyl salicylates, in which two bidentate ligand molecules are coordinated to the outer Tb(III) ion (the ligands shown in a green dotted circle in Fig. 1), and the others bridge two adjacent Tb(III) ions through phenolic oxygens (in a blue dotted circle). The apical Tb(III) ion has an anti-square prism geometry *via* $\mu_3$-OH bridges.

In contrast to similar cluster compounds reported so far, all the ligand molecules of TNS-He play the following key roles in the structure formation. As represented in Fig. 1 and Fig. 2, there are two types of phenyl–phenyl interactions in a cluster unit: phenyl groups in hexyl salicylates binding to outer Tb(III) ions give C–H-π interactions ($d$ = 2.75–3.03 Å) in a nearly orthogonal relationship to each other (Fig. 2(b)), whereas the others take part in the *J*-type π-π stacking of proximate phenyl groups around the cluster (Fig. 2(a)). Those four couples of adjacent phenyl stackings lie parallel with a mean distance $d$ = 3.482–3.599 Å, which is close enough to extensively contact each other. Thus, both the π-π stackings and C–H-π interactions around the Tb(III) hydroxo cluster core make the inorganic–organic hybrid more rigid. The specific two-way phenyl ring contacts might be induced in the hydrophobic environment formed by long alkyl chains of assembled hexyl salicylate ligands.

In Fig. 3, absorption spectra of both clusters in methanol ([clusters] = 1 × $10^{-5}$ M) are illustrated.[9] Notably, a peak at around 315 nm for TNS-Me assigned to the π-π* absorption transition of the carbonyl group was not observed in TNS-He. The approximately 25 nm red-shift of the band for TNS-He is probably due to the formation of stabilized *J*-type π-π stackings.[10] The longer alkyl chains of TNS-He are considered to afford a more hydrophobic environment to help effective phenyl–phenyl interactions. This can explain the more pronounced bathochromic effect compared with those in TNS-Me. In addition, the TNS-He has high molar extinction coefficients with a maximum value of around 60 000 dm$^3$ mol$^{-1}$ cm$^{-1}$ at 340 nm, which is apparently higher than those of TNS-Me. It should be noted that the TNS-He has relatively high ε values in a violet light region (*e.g.* λ = 380 nm, ε = 9000 dm$^3$ mol$^{-1}$ cm$^{-1}$).

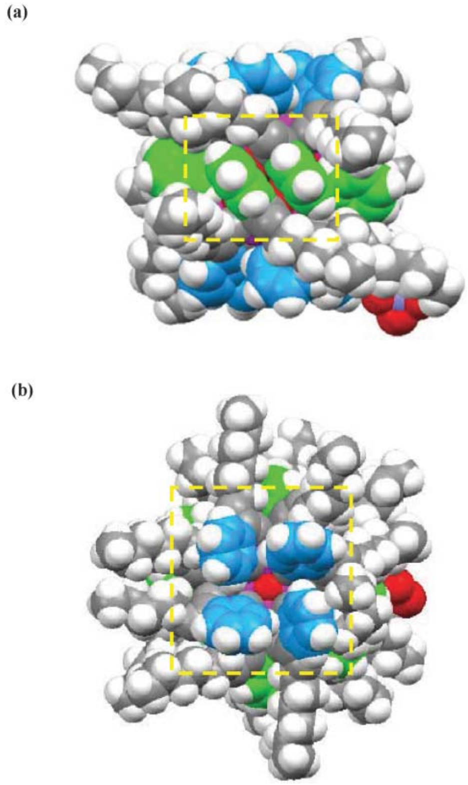

**Fig. 2** Space-filling mode of TNS-He: side view (a) and top view (b). The two phenyl interactions, π-π stacking (green) and C–H-π interactions (blue) are emphasized, respectively.

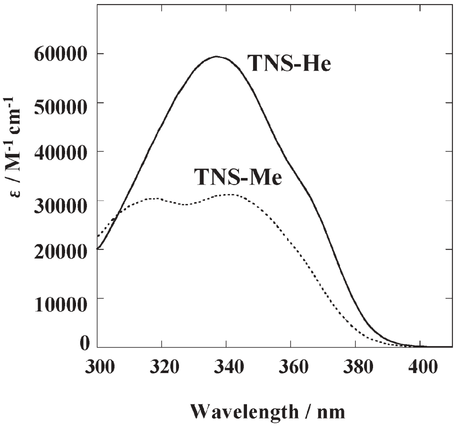

**Fig. 3** Absorption spectra of TNS-He and TNS-Me in methanol. [Clusters] = 1 × $10^{-5}$ M.

The emission spectra of clusters in methanol are also depicted in Fig. 4. Excitation at 380 nm gives rise to characteristic 4f-4f bands of Tb(III) ions with a most intense peak at 545 nm ($^5D_4 \rightarrow {}^7F_5$) for both clusters. The more remarkable stronger emission was observed for TNS-He, in which the $^5D_4 \rightarrow {}^7F_5$ intensity is seven times higher than that of the methyl ester analogue. Similarly, in a solid state, the luminescence is more striking than that of TNS-Me. Thus, more effective *J*-type π-π contacts for TNS-He may result in the stronger Tb(III) emisssion. We also found that the relative emission efficiency of TNS-He/TNS-Me is 3.0, based on the peak integral of emission intensity normalized by ε values. In our study, multiple ligand–ligand stabilizations could play crucial roles, *i.e.* in realizing longer wavelength sensitization of Tb(III) and in

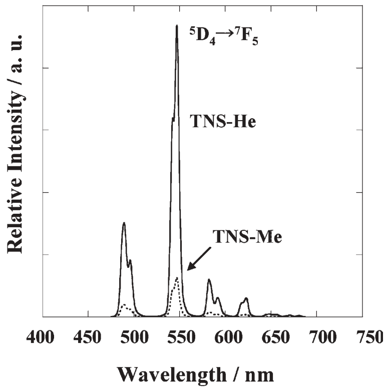

**Fig. 4** Emission spectra of TNS-He and TNS-Me in methanol. $\lambda_{\text{ex}}$ = 380 nm, [clusters] = 1 × $10^{-5}$ M.

rigidifying Tb(III) coordination sites to demonstrate more efficient Tb(III) luminescence of TNS-He. To our knowledge, no clear indications have been made regarding the importance of ligand–ligand interactions, which are linked to lanthanide(III) photosensitised luminescence.[11]

In conclusion, the remarkable photoluminescence of TNS-He in both crystalline state and in solution was rationalized as being due to the rigid core structure through the phenyl ring interactions of *J*-type π-π stackings and C–H-π interactions, and through the hexyl group interactions of the sixteen pairs of coordinating hexyl salicylates. The self-organized salicylates, as the energy-transfer sensitizing site to Tb(III) ions, play important roles both in red shift of the absorption maximum (25 nm) and the increased absorption coefficient (ε values). The photoexcitation at 380 nm ($\varepsilon = 9000$ dm$^3$ mol$^{-1}$ cm$^{-1}$, [cluster] = $1 \times 10^{-5}$ M) led to efficient energy transfer, in other words, the photosensitized luminescence of the Tb(III) cluster. To our knowledge, this is the first observation of the remarkable lanthanide(III) photoluminescence based on photosensitization from multiple ligand–ligand interaction states.

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## Notes and references

‡ Crystallographic data: TNS-He, $M = 5202.76$, tetragonal, $a = 24.505(2)$, $c = 36.170(3)$ Å, $U = 21720.6(31)$ Å$^3$, $T = -180$ °C, $D_{\mathrm{cal}} = 1.610$ g cm$^{-3}$, $P4_2/n$, $Z = 4$, $\mu$(Mo K$\alpha$) = 29.636 cm$^{-1}$. Measurements were made on a Rigaku RAXIS RAPID imaging plate area detector. The final cycle of full-matrix least squares refinement was based on 19 864 observed reflections and 1232 variable parameters, and converged with unweighted and weighted agreement factors of $R_1 = 0.0446$ and w$R_2 = 0.1241$. CCDC 626753. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b616387d

§ Syntheses and characterizations of TNS-Me and TNS-He. Methyl salicylate (0.600 g, 3.94 mmol) was dissolved in methanol and triethylamine (0.648 g, 6.41 mmol) was added to this solution with stirring at 40 °C. Then, $Tb(NO_3)_3 \cdot 6H_2O$ (1.00 g, 2.22 mmol) in methanol was added dropwise to this solution with further stirring for 20 min. White powder (TNS-Me) was obtained. The cluster, TNS-He, was synthesized in a way similar to that of TNS-Me by using hexyl salicylate. For $Tb_9(Hesa)_{16}(\mu\text{-}OH)_{10}(NO_3)$ (Hesa: hexyl salicylate) ($C_{208}H_{282}O_{61}NTb_9$). Calculated: C, 48.01%, H, 5.46%, N, 0.3%. Found: C, 47.99%, H, 5.35%, N < 0.3%. Selected IR (KBr, cm$^{-1}$): 1382($NO_3$). FABMS: *m*/*z* 5140 $[Tb_9(Hesa)_{16}(OH)_{10}]^+$. For $Tb_9(Mesa)_{16}(\mu\text{-}OH)_{10}(NO_3)$ (Mesa: methyl salicylate) ($C_{128}H_{122}O_{61}NTb_9$). Calculated: C, 37.67%, H, 3.01%, N, 0.3%. Found: C, 37.26%, H, 3.20%, N, 0.8%. Selected IR (KBr, cm$^{-1}$): 1382($NO_3$). FABMS: *m*/*z* 4018 $[Tb_9(Mesa)_{16}(OH)_{10}]^+$. From the X-ray analysis of TNS-He and these characterizations, it is reasonable to conclude that both clusters have similar nonanuclear Tb(III) structures.

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