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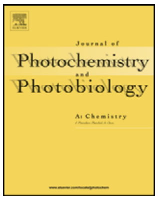

Synthesis and characterization of photoluminescent terbium-containing polymer precursors

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Two new ternary Tb^{3+} complexes, $Tb(MAA)_3$phen and $Tb(AA)_3$phen have been synthesized that possess polymer precursors. Each complex consists of two different ligands: one is carboxylate which is derived from methacrylic acid (MAA) or acrylic acid (AA) to serve not only as a ligand but also as a functional group for polymer precursor, the other is 1,10-phenanthroline which is found to be a critical component to make the complex exhibit desirable photophysical properties. The fluorescence of the complexes shows the characteristic emission of Tb^{3+} ion in both solid state and liquid solution. The fluorescence intensity is found to be concentration-dependent in solution up to 0.02 M. Afterwards, the emission property of $Tb(AA)_3$phen shows to be fairly stable all the way up to 0.1 M.

1. Introduction

Photoluminescence of rare earth metal complexes has been the subject of intensive investigation due to the unique photophysical features such as narrow emission bands, large stokes shift, and long luminescence decay time [1,2]. These highly desirable properties are actively sought for numerous applications, including display devices, chemical and biological sensors, and optical communications [3–7]. Currently, there are two approaches to the material development. One is the use of host–guest system in which the metal complexes are dispersed in polymeric matrices [8–11]. The other is to covalently embed the metal-containing coordination chromophores to polymeric backbones [12]. The latter system has a unique capability in the prevention of phase separation and leaching of photoactive components, which are often associated with the host–guest system.

The system with such advantages can be developed in two routes. One involves the use of a functional polymer to react with a metal salt [13] while the other directly polymerizes a metal-containing precursor [14,15]. The latter route particularly offers a well-defined structure around the metal center, which, in turn, leads to the well-defined photophysical properties. In contrast, it is always difficult to determine the precise central coordination environment for all the metal centers when functional polymers are used in the first place due to the fact that a polymer chain could be tangled. Functional group availability and metal access inevitably become an issue. The resultant ionic aggregates tend to lead to serious emission quenching even at low rare earth content [13]. In addition, the luminescence is highly sensitive to environment of the metal center [16,17]. Without a preconditioned coordination, it will certainly complicate elucidation of photophysical optical properties. For these reasons, the metal-containing precursors have been highly desirable although the development is known to be challenging [18]. Here we disclose that two new Tb(III)-containing precursors have been developed and fully characterized. Most importantly, the obtained precursors are already luminescent.

2. Physical measurements and materials

Tb_4O_7 (99.99 wt%) was purchased from LuoDiya Fangzheng Rare Earth New Material Ltd. N,N-Dimethylformamide (DMF), methacrylic acid (MAA), acrylic acid (AA) and 1,10-phenanthroline (phen) were purchased in analytical grade from Medicine Group Shanghai Chemicals Company. DMSO was purchased in analytical grade from Dongyi Chemicals Company.

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Elemental analysis of C, H, N contents was carried out with a PerkinElmer Series II CHNS/O 2004 elementary analyzer. The content of Tb^{3+} was analyzed by gravimetric determination. IR spectra were obtained on Bruker TENSOR27 FTIR spectrometer using KBr discs in 4000–400 cm^{-1}. Electronic spectra were analyzed on a Hitachi UV-2501 fluorometer. Samples were dispersed by ultra-sonoscope prior to test. Thermogravimetric analysis (TG) and differential thermogravimetric analysis (DTG) for thermal properties were recorded on the Netzsch STA 409PC synchronous thermal analyzer under N_2 atmosphere, with elevation rate of temperature of 10 °C/min. Fluorescence spectra were measured on a Hitachi RF-5300 fluorimeter (slit *D* 2.5 nm with the excited and emission scanning range between 200 and 800 nm at 36 ± 0.5 °C). Quartz cuvettes with 1 cm optical path length are used for solution UV–vis and fluorescence measurement. For solid fluorescence, powder samples are sandwiched between two quartz slides, and mounted in such a way that emission is detected at right angle.

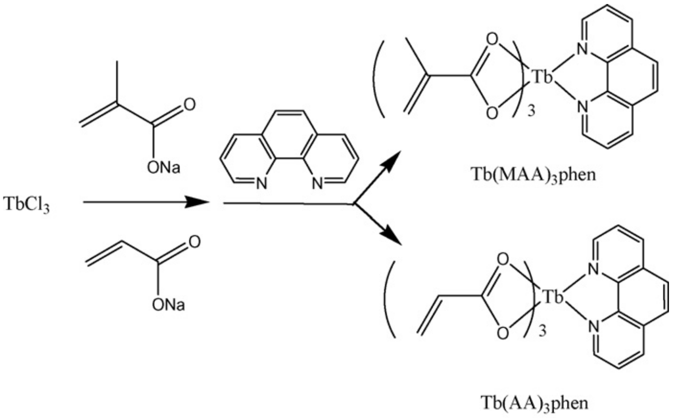
3. Experimental

Tb_4O_7 (10 mmol) was added into 50 mL HCl solution with magnetic stirring until the solution turns transparent. Hydrogen peroxide solution (2 mL, 15 wt%) was then added. The mixture was stirred for 1.5 h and then distilled under reduced pressure to remove the solvent. To the residue was added 100 mL alcohol (99.5%) to generate the $TbCl_3$–alcohol solution. Sodium acrylate solution with pH 6.5, freshly prepared by the treatment of acrylic acid (120 mmol) with NaOH (120 mmol) was added into the $TbCl_3$–alcohol solution. After the mixture was stirred for another 2.5 h, the white precipitate was filtered off. To the filtrate was dropwise added 1,10-phenanthroline–ethanol solution (40 mmol) with vigorous stirring. Upon the addition, white solids began to form. After the completion of addition, the mixture remained stirred for 3 h. The precipitate was then collected and washed with water, followed with ethanol. Recrystallization from ethanol (75 wt%) gave pure $Tb(AA)_3phen$ complex which was filtered off upon standing for 12 h, washed with distilled water and then ethanol, dried at 80 °C in vacuum for 2 h. The yield is 70–75%.

$Tb(MAA)_3phen$ was prepared in the same fashion except using MAA to replace AA.

4. Results and discussion

The synthesis of Tb complexes was achieved by using two different ligands in a tandem process, first AA or MAA and then phen (Scheme 1). It involves treatment of freshly prepared $TbCl_3$ with sodium salt of AA or MAA, followed by the addition of phen. The formed complexes possess characteristic fluorescence property of the rare earth metal. The presence of phen was found to be the key to such property. The precipitate collected from the mixture of $TbCl_3$ and sodium salt of AA did not show any fluorescence when illuminated by ultraviolet light. Only after adding phen to the filtrate did the obtained complex showed the desirable rare earth metal fluorescence. These complexes have good solubility in DMF and DMSO. It is found that the solubility increases in these solvents with rising temperature. The complexes are insoluble in water, and only sparsely soluble in acetone, ethanol, CCl_4, and THF.



Scheme 1.

Table 1
Composition analysis of the complexes.

Element content	$Tb(AA)_3phen \cdot 1/4H_2O$ found (calc.)	$Tb(MAA)_3phen \cdot 1/4H_2O$ found (calc.)
C%	45.73 (45.30)	48.00 (48.13)
H%	3.10 (3.12)	3.96 (3.91)
N%	4.94 (5.03)	4.24 (4.68)
Tb%	28.48 (28.54)	26.58 (26.54)

The reaction under 1:3:1 (Tb(III):mono acid:phen) molar ratio is known to generate complexes with general formula of $Tb(O_2CR)_3phen$ [19a]. The present approach does lead to the predictable outcome. Elemental analysis results (Table 1) confirm the composition of complexes to be $Tb(AA)_3phen$ and $Tb(MAA)_3phen$, respectively. Each complex is associated with $1/4H_2O$ (vide infra). The content of Tb^{3+} was analyzed by gravimetric method. The residue obtained after the complexes were thermally processed in a muffle was analyzed by IR spectrum (Fig. 1). The comparison with the IR from an authentic sample indicates the residue to be Tb_4O_7 [19b].

IR spectra of both $Tb(AA)_3phen$ and $Tb(MAA)_3phen$ are shown in Fig. 2a and b, respectively, together with those of phen, AA, and MAA. The absorption peaks at 3429 and 3445 cm^{-1} belong to the intrachain hydrogen bond, possibly formed between carbonyl of the ligands (AA or MAA) and the hydroxyl of lattice water [20]. The broad υ_{O-H} absorption band at 2500–3450 cm^{-1} for free acids disappears upon complexation, indicative of deprotonation of the acid group. The carbonyl absorption for free acrylic acid and methacrylic acid is at 1705 and 1697 cm^{-1}, respectively. They are absent from both complexes, suggesting the participation by the carbonyl oxygen in coordination [21a]. The emergence of two bands at 1581 and 1430 cm^{-1} for Tb $(AA)_3phen$ arises from antisymmetric and symmetric vibrational stretching modes for delocalized carboxylate, which are typically found to be in the range of 1400–1600 cm^{-1} [21b]. The separation of the two bands ($\Delta\upsilon_{(OCO)} = \upsilon_{as} - \upsilon_s$) around

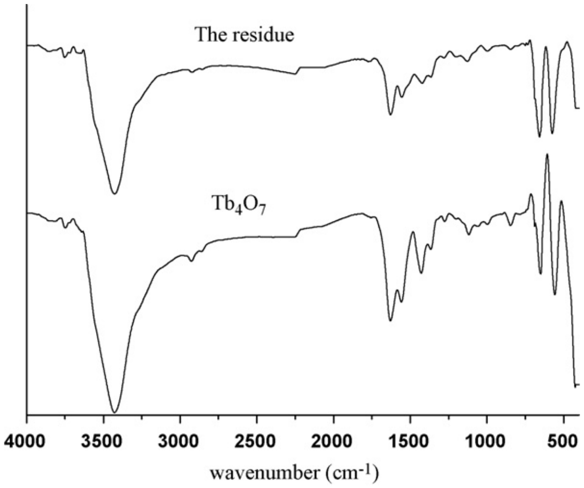


Fig. 1. IR spectra of the residue and authentic Tb_4O_7.

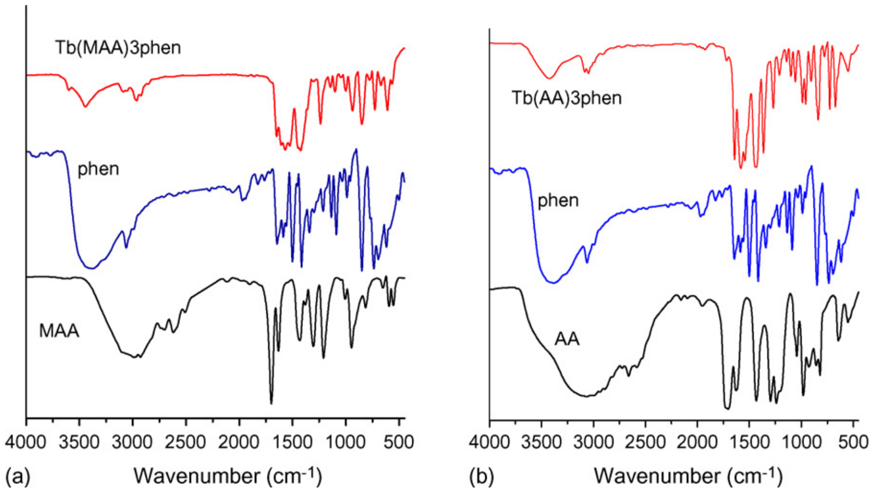


Fig. 2. IR spectra of Tb(AA)$_2$phen and Tb(MAA)$_2$phen as well phen, MAA and AA.

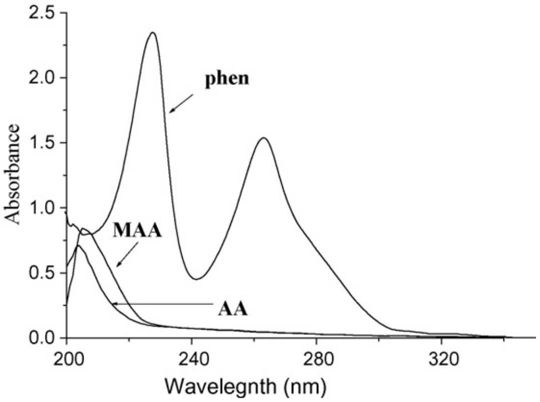


Fig. 3. UV–vis of ligands (concentrations: 3 × 10^{-4} M).

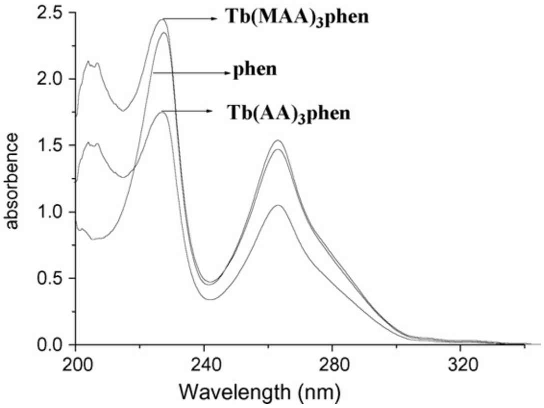


Fig. 4. UV–vis of complexes and 1,10-phenanthroline (concentrations: 3 × 10^{-4} M).

151 cm^{-1} conforms to bidentate functionality of the carboxylate. The value is in agreement with those from other terbium carboxylate complexes [21c,21d]. Two similar bands are found at 1569 and 1425 cm^{-1} for Tb(MAA)$_3$phen with the $\Delta\upsilon_{(OCO)}$ value at 144 cm^{-1}, again indicating that MAA serves as a bidentate ligand as AA does. Characteristic phen absorption peaks are found at 1542, 1513, and 1452 cm^{-1} in Tb(AA)$_3$phen, and 1613, 1526, and 1454 cm^{-1} in Tb(MAA)$_3$phen, respectively. Compared with free phen [22], these absorptions are shifted due to complexation. In addition, the ω_{C-H} wagging vibration peaks of phen [22] at 852 and 737 cm^{-1} further move to 837 and 725 cm^{-1} in Tb(AA)$_3$phen, and 849 and 728 cm^{-1} in Tb(MAA)$_3$phen, respectively. The results are comparable to observation from other phen-containing terbium complexes [23].

The UV absorption (Fig. 3) of the ligands appears at 203 nm for AA and 205 nm for MAA, respectively, characteristic of carbonyl absorption. The free ligand phen has two bands, one at 227 nm for the π–π^* absorption and the other at 263 nm for n–π^* absorption.

Both complexes in ethanol show similar UV spectra (Fig. 4) with absorptions at 263 and 227 nm characteristic of phen. There is an absorption peak at 205 nm due to the red-shift of double bond absorption from phen [24].

The TG and DTG analyses were showed in Figs. 5 and 6, respectively, and thermal data of DTG and DSC (differential scanning calorimetry) were listed in Table 2. The on-set decomposition temperature is 310 °C for Tb(AA)$_3$phen vs. 282.8 °C for Tb(MAA)$_3$phen. Thermal stability for Tb(AA)$_3$phen is better than that of Tb(MAA)$_3$phen although the overall thermal stability for both complexes is excellent. The observation of slightly lower thermal stability for Tb(MAA)$_3$phen is ascribed to aliphatic nature of methyl group in MAA [25].

There were two thermal decomposition steps for Tb(AA)$_3$phen (Fig. 5), corresponding to the two peaks in DTG at 325.4 and 449.8 °C, respectively. Three thermal decomposition steps were found for Tb(MAA)$_3$phen (Fig. 5), with corresponding DTG peaks at 303.1, 382.9, and 468.6 °C. The maximum weight loss rate occurred at 352.4 °C for Tb(AA)$_3$phen, and 382.9 °C for Tb(MAA)$_3$phen, respectively. In addition, there is no occurrence of any other thermal activity prior to the decomposition of the complexes, suggest-

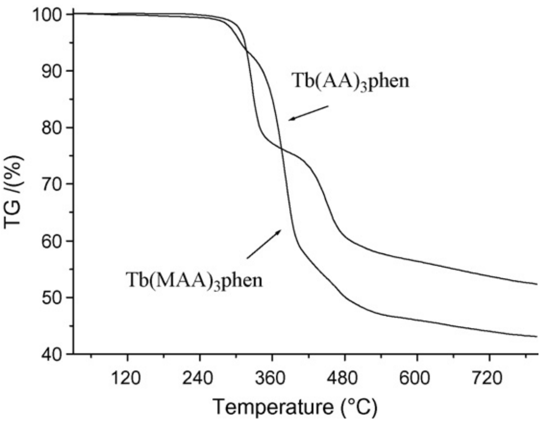


Fig. 5. TG of complexes.

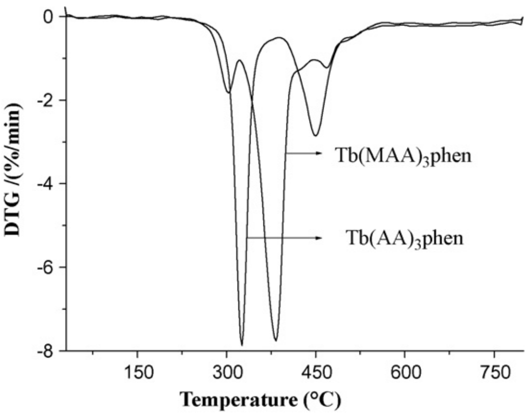


Fig. 6. DTG of complexes.

Table 2
Thermal decomposition data of the complexes.

Sample	$Tb(AA)_3phen$	$Tb(MAA)_3phen$
On-set decomposition temperature (°C)	310.0	282.8
Peak value of DTG (°C)	325.4, 449.8	303.1, 382.9, 468.6
Peak value of DSC (°C)	317.7, 321.1, 460.3	292.0, 326.2, 378.9, 472.0

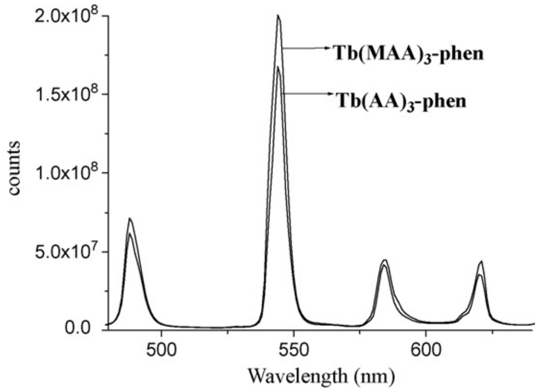


Fig. 7. Emission spectra of solid complexes in powder (λ_{ex} = 346 nm).

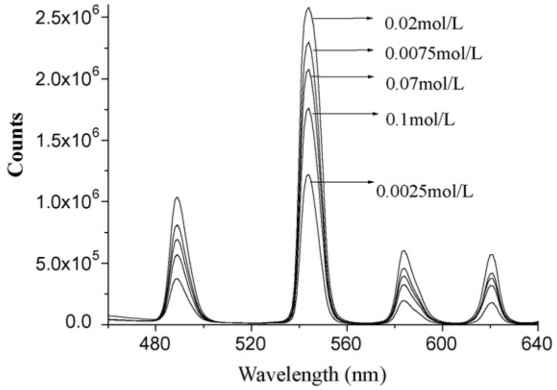


Fig. 8. The emission intensity change of $Tb(MAA)_3phen$ in DMSO solution (λ_{ex} = 346 nm).

ing that there is no fusing reactivity in these complexes under these thermal conditions [26]. The thermal stability has been also examined with derivative thermal analysis. Clearly, the results are consistent with the notion that both complexes are highly thermally stable.

The luminescence properties in solid state and in DMSO solution have been investigated. The properties of Tb(III) complexes are manifested despite the fact that Tb(III) ion has low extinction coefficient. The key is to use ligands for harvesting light, an approach known as "antenna effect". Phen, among others has been explored to sensitize the metal center [27–30]. We have used phen and found that such sensitizers are necessary. The excitation parameters and the emission results are listed in Table 3. The emission spectra from the solid state for both complexes and from DMSO solution for $Tb(MAA)_3phen$ are shown in Figs. 7 and 8, respectively. In both states, the complexes exhibit characteristic emission of the rare earth metal Tb^{3+} with peaks corresponding to ($^5D_4$–$^7F_6$), ($^5D_4$–$^7F_5$), ($^5D_4$–$^7F_4$), and ($^5D_4$–$^7F_3$) transitions. Among them, the most intense emission peak is at ca. 544 nm ($^5D_4$–$^7F_5$). The excitation wavelengths needed for the solid samples are found to be generally shorter than those for the DMSO solution (Table 3), suggesting that a lower excitation energy is sufficient for the solution samples. It is ascribed to the response to intermolecular interaction. Molecules in solution state have weaker interaction than in solid state because of distance-dependent diffusion process in solution. When molecules are in the solid state, the electronic transition was confined by crystal lattice so that the electronic transition energy and the excitation energy increase. On the other hand, the emission of $Tb(MAA)_3phen$ is slightly more intense than that of $Tb(AA)_3phen$ in solid state (Fig. 7), possibly due to the steric effect by methyl group which reduces intermolecular interaction. As a result the vibration excited state energy dissipation is reduced and the emission intensity is increased [31].

Concentration-dependent emission for $Tb(MAA)_3phen$ has been examined over the range of concentrations from 0.0025 to 0.1 M. The wide concentration range including high upper concentration is investigated to determine the optimal fluorophore loading. High upper concentration is used out of consideration of importance for the future reference in polymeric photoluminescence material development. Although there is no emission shift, the emission intensity does respond accordingly, with the most intense emission observed at 0.02 M (Figs. 8 and 9). Further increase in the concentration (up to 0.1 M) leads to a decrease in emission intensity.

Fig. 10 shows the relationship between emission intensities and concentrations for $Tb(AA)_3phen$. For $Tb(MAA)_3phen$, when the concentration exceeds 0.02 M, quenching occurs with decrease of emission intensities across the spectrum. However, for $Tb(AA)_3phen$, the intensity is eventually leveled off after 0.02 M. The exact mechanism is yet to be understood for the surprisingly marked difference. Usually, increase in concentration leads to one of the two things. One is to form excimers, and the other is to

Table 3
Fluorescence data from both solid and solution states.

		λ_{ex}(nm)	$^5D_4$–$^7F_6$	$^5D_4$–$^7F_5$ λ_{em}	$^5D_4$–$^7F_4$ (nm)	$^5D_4$–$^7F_3$
$Tb(MAA)_3phen$	In DMSO	346	488	544	584	621
	Powder	232				
$Tb(AA)_3phen$	In DMSO	353				
	Powder	236				

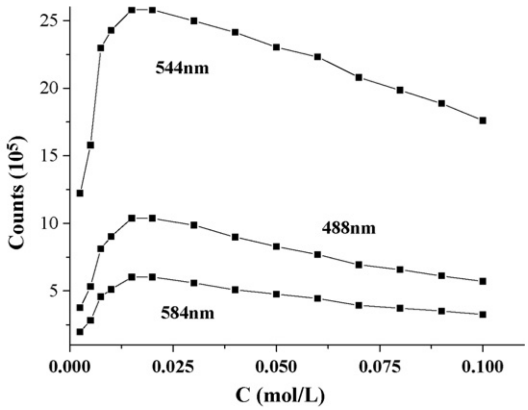


Fig. 9. The relationship between the emission intensity and the concentrations of $Tb(MAA)_3$phen in DMSO solution.

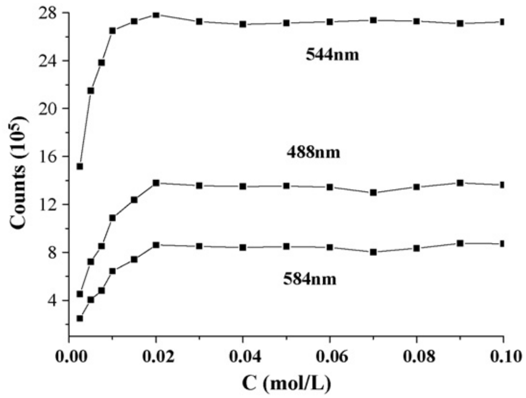


Fig. 10. The relationship between the emission intensity and the concentrations of $Tb(AA)_3$phen in DMSO solution.

have self-quenching. The former results from the interaction of an excited species with a neutral one leading to the formation of a new excited species. The latter could result from several possible processes including collisional quenching, static quenching, and combination of both [32]. Any of them or combination of two could be responsible for quenching in the present complexes. In addition, increased optical density or turbidity could also lead to the decrease in fluorescence intensity [32]. Both $Tb(MAA)_3$phen and $Tb(AA)_3$phen would be expected to behave similarly no matter which quenching mechanism plays in because of obvious similarity of structure. The only difference is the presence or absence of a methyl group. The fact that an increase in concentration over 0.02 M led to decrease in fluorescence for $Tb(MAA)_3$phen but not for $Tb(AA)_3$phen prompted us to speculate that the stretching and twisting motions from flexible alkyl methyl group in $Tb(MAA)_3$phen may be responsible for the energy loss [33].

5. Conclusion

Two new Tb^{3+} complexes have been prepared, and each complex possesses two different motifs of ligands. One is MAA or AA-based which not only serves as ligands but also offers functional groups for polymer precursors. The other is 1,10-phenanthroline which is a key component for photophysical properties of the complexes. Characteristic photoluminescence properties of Tb(III) have been evaluated in both solid and solution states. The most intense emission peak is found at ca. 544 nm from $^5D_4$–$^7F_5$ transition. Concentration-dependent fluorescence study reveals a very interesting phenomenon that both $Tb(MAA)_3$phen and $Tb(AA)_3$phen behave differently in the range of over 0.02 M. Most importantly, the intensities of $Tb(AA)_3$phen remain almost constant after reaching the maximum. This photoluminescence stability offers not only a wide window for practical consideration for potential applications but also an insight into molecular design of advanced systems. Thermal stability study indicates that these complexes are highly thermally stable. These complexes, being incorporated with AA or MAA moieties have been used as polymer precursors for Tb(III)-containing polymers in which the metal centers are preconditioned with coordination chromophores. The preliminary study shows that the prepared co-polymers with methyl methacrylate possess characteristic terbium(III) emissions. It is obtained without the use of any additional sensitizers, indicative of the preconditioned phen effectively functioning as sensitizers. The full and detailed results will be reported in due course.

Acknowledgments

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References

[1] K. Kuriki, Y. Koike, Y. Okamoto, Chem. Rev. 102 (2002) 2347–2356.
[2] C. Yan, H. Dai, C. Guo, P. Lu, W. Wang, M. Zhang, G. Qiu, J. Rare Earths 25 (Suppl. 1) (2007) 20–23.
[3] M.D. McGehee, T. Bergstedt, C. Zhang, A.P. Saab, M.B. Oregan, G.C. Bazan, V.I. Srdanov, A.J. Heege, Adv. Mater. 11 (1999) 1349.
[4] C. Piguet, J.C.G. Bunzli, G. Bernardinelli, G. Hopfgartner, A.F. Williams, J. Am. Chem. Soc. 115 (1993) 8197.
[5] (a) M. Kawa, J.M. Frechet, J. Chem. Mater. 10 (1998) 286;
(b) H.G. Liu, Y. Lee, W.P. Qin, K. Jang, S. Kim, X.S. Feng, J. Appl. Polym. Sci. 92 (2004) 3524;
(c) Y. Hasegawa, M. Yamamuro, Y. Wada, N. Kanehisa, Y. Kai, S. Yanagida, J. Phys. Chem. A 107 (2003) 1697–1702.
[6] M. Elbanowshi, B. Makowska, J. Photochem. Photobiol. 99 (1996) 85.
[7] A.K. Saha, K. Kross, E.D. Kloszewski, D.A. Upson, J.L. Toner, R.A. Snow, C.D.V. Black, V.C. Desai, J. Am. Chem. Soc. 115 (1993) 11032.
[8] N.E. Wolff, R.J. Pressly, Appl. Phys. Lett. 2 (1963) 152–154.
[9] E. Banks, Y. Okamoto, Y. Ueba, J. Appl. Polym. Sci. 25 (1980) 359.
[10] H. Rudmann, S. Shimada, M.F. Rubner, J. Am. Chem. Soc. 124 (2002) 4918–4921.
[11] H. Jiu, J. Ding, Y. Sun, J. Bao, C. Gao, Q. Zhang, J. Non-Cryst. Solids 352 (2006) 197–202.
[12] R. Shunmugam, G.N. Tew, J. Am. Chem. Soc. 127 (2005) 13567–13572.
[13] Y. Okamoto, Y. Ueba, N.F. Dzhanibekov, E. Banks, Macromolecules 14 (1981) 17–22.
[14] L.-H. Wang, W. Wang, W.-G. Zhang, E.-T. Kang, W. Huang, Chem. Mater. 12 (2000) 2212–2218.
[15] B. Yan, L. Zhao, J. Liu, J. Photochem. Photobiol. A: Chem. 199 (2008) 50–56.
[16] (a) N. yoshino, S. Paoletti, J. Kido, Y. Okamoto, Macromolecules 18 (1985) 1513–1515;
(b) H. Lulan-Upton, Y. Kamot, A.D. Walser, J. Polym. Sci. A: Polym. Chem. 38 (1997) 393–398.
[17] C. Du, L. Ma, Y. Xu, Y. Zhao, C. Jiang, Eur. Polym. J. 34 (1998) 2329.
[18] Y. Ueba, K.J. Zhu, E. Banks, Y. Okamoto, J. Polym. Sci., Part A 20 (1982) 127.
[19] (a) Y. Fu, J. Zhang, Z. Huang, X. Wang, Y. Lu, W. Cao, J. Photochem. Photobiol. A: Chem. 197 (2008) 329–334;
(b) Y. Chen, W. Cei, Chin. J. Rare Met. 6 (2005) 865–869.
[20] X.-L. Zhang, Chin. J. Struct. Chem. 27 (2008) 117–122.
[21] (a) Kazuo-Nakmoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Beijing Chemical Industry Press, 1986, pp. 237;
(b) J. Oomens, J.D. Steill, J. Phys. Chem. A 112 (2008) 3281–3283;
(c) E.E. Teotonio, H.F. Brito, M.C. Felinto, L.C. Thompson, V.G. Young, Oscar L. Malta, J. Mol. Struct. 751 (2005) 85–94;
(d) G.B. Deacon, R.J. Phillips, Coord. Chem. Rev. 33 (1980) 251.
[22] C. Makedonas, C.A. Mitsopoulou, Spectrochim. Acta Part A 64 (2006) 918–930.
[23] J. Yang, Q. He, et al., J. Chin. Rare Earths Soc. 24 (2006) 103–109.
[24] S. Yu, L. Li, Analysis Means of Spectrum, 2nd ed., Chongqing University Press, 1994.
[25] L.A. Berg, Differential Thermal Analysis, Academic Press, London, 1970, pp. 343.
[26] O.M. Khreis, R.J. Curry, M. Somertom, et al., J. Appl. Phys. 88 (2000) 777–780.
[27] J.-G. Kang, T.-J. Kim, H.-J. Kang, S.K. Kang, J. Photochem. Photobiol. A: Chem. 174 (2005) 28–37.
[28] V. Balzani, Photochem. Photobiol. Sci. 2 (2003) 459.

[29] (a) M.D. McGehee, T.B. Bergstedt, C. Zhang, A.P. Saab, M.B. O'Regan, G.C. Bazan, V.I. Srdanov, A.J. Heeger, Adv. Mater. 11 (1999) 1349;
(b) D. Parker, J.A.G. Williams, J. Chem. Soc., Perkin Trans. 2 (1996) 1581.

[30] (a) W. Hu, M. Matsumura, M. Wang, L. Jin, Appl. Phys. Lett. 77 (2000) 4271;
(b) Y. Zheng, J. Lin, Y. Liang, Q. Lin, J. Yu, Q. Meng, Y. Zhou, S. Wang, H. Wang, H. Zhang, J. Mater. Chem. 11 (2001) 2615.

[31] L.H. Wang, W. Wang, W.G. Zhang, J. Chin. Rare Earths Soc. 1 (2001) 91–94.

[32] J.R. Lakowicz, Principles of Fluorescence Spectroscopy, 2nd ed., Kluwer/Plenum, New York, 1999, pp. 237–247.

[33] N.J. Turro, Modern Molecular Photochemistry, University Press, Menlo Park, CA, 1978, p. 113.