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Synthesis, characterization and spectroscopic investigation of new *tetrakis*(acetylacetonato)thulate(III) complexes containing alkaline metals as counteractions

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ABSTRACT

In this work a series of *tetrakis* complexes $C[Tm(acac)_4]$, where $C^+ = Li^+, Na^+$ and K^+ counteractions and $acac = acetylacetonate$ ligand, were synthesized and characterized for photoluminescence investigation. The relevant aspect is that these complexes are water-free in the first coordination sphere. The emission spectra of the *tetrakis* Tm^{3+} -complexes present narrow bands characteristic of the ${}^1G_4 \rightarrow {}^3H_6$ (479 nm), ${}^1G_4 \rightarrow {}^3F_4$ (650 nm) and ${}^1G_4 \rightarrow {}^3H_5$ (779 nm) transitions of the Tm^{3+} ion, with the blue emission color at 479 nm as the most prominent one. The lifetime values (τ) of the emitting 1G_4 level of the $C[Tm(acac)_4]$ complexes were 344, 360 and 400 ns for the Li^+ , Na^+ and K^+ counteractions, respectively, showing an increasing linear behavior versus the ionic radius of the alkaline ion. An efficient intramolecular energy transfer process from the triplet state (T) of the ligands to the emitting 1G_4 state of the Tm^{3+} ion is observed. This fact, together with the absence of water molecules in first coordination sphere, allows these *tetrakis* Tm^{3+} -complexes to act as efficient blue light conversion molecular devices.

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1. Introduction

The great interest in research on the luminescence properties of trivalent rare earth (RE^{3+}) complexes containing β -diketonate ligands is mainly due to their potential applications such as medical diagnosis [1,2], electroluminescence [3], triboluminescence [4], optical markers [5] and laser materials [6]. The importance of photoluminescence properties of RE^{3+} ions is associated mainly with their narrow emission bands arising from the intraconfigurational 4f–4f transitions and long lifetimes, which make these ions unique among the luminescent coordination compounds [7].

The design of highly luminescent trivalent europium and terbium complexes containing β -diketonate ligands is the most intensively investigated among the RE^{3+} coordination compounds [8,9]. Great attention focused on the study of the optical properties of Eu^{3+} ($4f^6$) and Tb^{3+} ($4f^8$) ions is mainly due to their practical applications as red and green luminescence emitters, respectively [10–12]. On the other hand, less attention has been dedicated to the investigation of trivalent thulium complexes that exhibit blue color emission. The Tm^{3+} ($4f^{12}$) complexes usually

show only very weak 4f–4f luminescence, as a consequence of the small energy gap between their emitting and lower energy levels; this increases the probability of non-radiative transitions through coupling with vibrational modes in the ligands [9]. However, Tm^{3+} ion presents intraconfigurational ${}^1G_4 \rightarrow {}^3H_6$ transition, exhibiting blue emission color at about 480 nm, which when combined with the Tb^{3+} (green) and Eu^{3+} (red) ions may result in full-color emission phosphors [13,14]. In the last decades there has been a great interest in full-color systems, due to their enormous technological potential both for displays and for lighting devices [15]. In general, the literature [16–22] has focused on the spectroscopic study of systems containing the Tm^{3+} ion formed by different inorganic matrices.

The main type of RE^{3+} β -diketonate complexes reported in the literature [8,9] is the *tris*(β -diketonate) with the general formula $[RE^{3+}(\beta\text{-diketonate})_3 \cdot (H_2O)_x]$, where there are 3 β -diketonate anions for each RE^{3+} ion and x water molecules in the first coordination sphere that act as luminescence quenchers. Yet another approach is to arrange 4 β -diketonate ligands around an RE^{3+} ion, resulting in an anhydrous *tetrakis*(β -diketonates) system with the formula $C[RE(\beta\text{-diketonate})_4]$, where $C^+ = counteraction$. The counteraction (C^+) can be an alkali-metal (Li^+ , Na^+ , K^+ , Cs^+ and Rb^+) or a protonated organic base (pyridinium, piperidinium, isoquinolinium, etc.) [8]. This *tetrakis* system containing the β -diketonate anions acts as a bidentate ligand that has preference

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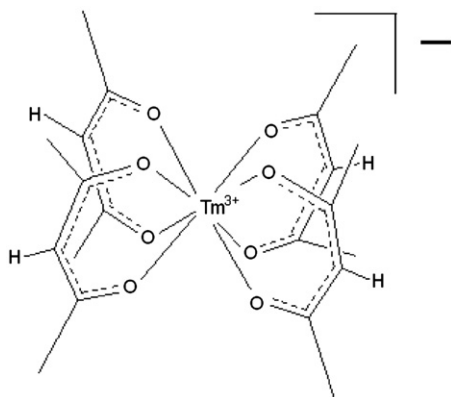


Fig. 1. Structural formula anion complex in the $C^+[Tm(acac)_4]^-$ compounds ($C^+ = Li^+, Na^+$ and K^+).

for the stereochemistry of 8 coordinated complexes, forming highly stable compounds. Therefore, the first coordination sphere in the *tetrakis*(β -diketonates) complexes is saturated, shielding the entrance of water molecules that quench the luminescence of the rare earth ions (Fig. 1).

In addition, the altering of the C^+ counteranions in the $C[RE(\beta\text{-diketonate})_4]$ complexes changes the structure of the complex, in particular the local coordination geometry of the metal ion and consequently its optical properties [23]. The complexes with ratio 4:1 of diketonate anions to RE^{3+} ions (*tetrakis*-complex) have one more diketonate ligand than the *tris*-complex (3:1), resulting in overall higher UV absorption cross section, and consequently blue emission intensity. It is worth mentioning that generally the synthesis of *tetrakis* RE^{3+} -complexes is more difficult than that with *tris* RE^{3+} -compounds.

This work reports on the synthesis, characterization and photoluminescence properties of thulium *tetrakis*(acac) complexes $C[Tm(acac)_4]$, where $C^+ = Li^+, Na^+$ and K^+ ; acac=acetylacetonate. Blue emission color at room temperature is observed for three thulium *tetrakis*(acac) complexes. The CIE color coordinates (x,y) from the emission spectra were determined.

2. Experimental

The following commercially available chemicals were used without further purification: acetylacetone, LiOH, NaOH and KOH were purchased from Merck while the Tm_2O_3 from Rhodia. The thulium chloride was prepared from thulium oxide and hydrochloric acid. The homogeneous solution was heated ($\sim 80^\circ C$) with stirring and HCl was added dropwise until $pH \sim 6.0$. The solution obtained was filtered and evaporated in a water bath leading to crystalline $TmCl_3 \cdot 6H_2O$ compound. The crystals were dried under reduced pressure over a blue silica gel.

2.1. Preparation of the $C[Tm(acac)_4]$ complexes

First, to deprotonate the acetylacetone ligand (Hacac), an aqueous solution of its respective lithium hydroxide (17.5 mmol in 10 mL of water) was added to a solution of acetylacetone (1.75 g, 17.5 mmol) dissolved in 20 mL of ethanol (95%), with stirring. Then, to this homogeneous mixture was added the thulium chloride ethanol solution (1.34 g, 3.5 mmol in 10 mL of EtOH), resulting in the formation of a white precipitate of $Li[Tm(acac)_4]$ complexes. After stirring for 4 h at room temperature, the mixture was cooled in the refrigerator overnight. The solid product was filtered, washed with water and dried under

reduced pressure for 12 h. It is worth mentioning that the same preparation procedure was used to prepare the other two *tetrakis*-complexes with Na^+ and K^+ counteranions. All three $C[Tm(acac)_4]$ complexes are stable in air, non-hygroscopic and insoluble in common organic solvents such as acetone, DMSO, acetonitrile, chloroform and ethanol.

The carbon and hydrogen percentages in the complexes were determined from elemental analyses, using a Perkin–Elmer Model 240 microanalyzer.

Thermal analysis was performed on a thermobalance Hi-RES TGA 2950TA instrument. The Tm^{3+} -complexes were placed in platinum containers, and the TG curves were recorded in dynamic synthetic air atmosphere of $50\text{ cm}^3\text{ min}^{-1}$ at a heating rate of $5^\circ C\text{ min}^{-1}$ in the temperature range from 25 to $900^\circ C$.

XRD patterns of the powders were recorded on a Rigaku Miniflex diffractometer using $Cu\ K\alpha$ radiation (30 kV and 15 mA) from 2° to 90° and 1 s of pass time.

Infrared spectra were recorded in KBr pellets on a Bomem model MB-102 spectrophotometer in the range from 350 to 4000 cm^{-1} , to obtain information on ligand- Tm^{3+} coordination. In addition, near-infrared absorption spectra of the Tm^{3+} coordination compounds were recorded at room temperature in a Nicolet Magna 850 spectrophotometer, in the spectral range from 710 to 2100 nm, in order to get information on the low energy $4f\text{--}4f$ transitions of the rare earth ion.

Steady-state excitation spectra of the Tm^{3+} complexes in solid state at room temperature were recorded at an angle of 22.5° (front face) with a spectrofluorimeter (SPEX-Fluorolog 2) with double grating 0.22 m monochromator (SPEX 1680), and a 450 W xenon lamp as excitation source. All spectra were recorded using a detector mode correction. The experimental conditions were exactly the same for both the systems (excitation wavelength, sample position, slit widths, etc.).

The emission spectra were also measured at room temperature, in the range from 450 to 850 nm, on excitation at 325 nm, using a He–Cd laser pump. The luminescence signals were filtered by a simple (0.3 m) monochromator, collected by an R928 photomultiplier detector and amplified by a lock-in Stanford Research model SR830. Excited states lifetime measurements were made using a third harmonic of Continuum Q-Switch Nd:YAG laser (10 ns). The signals were recorded by an R928 photomultiplier coupled to the Tektronix TDS380 digital oscilloscope.

3. Results and discussion

The chemical compositions of the Tm^{3+} -complexes, determined by the CHN elemental analysis in percentages, found for the respective alkaline metal counteranions, were as follows: for Li^+ – elemental analysis calculated: C, 41.97%; H, 4.93%; found: C, 41.75%; H, 4.71%; for Na^+ – elemental analysis calculated: C, 40.83%; H, 4.80%; found: C, 40.74%; H, 4.52% and for K^+ – elemental analysis calculated: C, 39.74%; H, 4.67%; found: C, 39.54%; H, 4.35%. These results indicate the general formula $C[Tm(acac)_4]$.

The infrared spectra (figure not shown) of the $C[Tm(acac)_4]$ complexes presented the displacement of the $\nu_s(C=O)$ stretching from 1624 cm^{-1} in the free acac ligand to 1605, 1600 and 1595 cm^{-1} for the *tetrakis* Tm^{3+} -complexes, with Li^+, Na^+ and K^+ , respectively. Besides, the $\nu_s(C\cdots C)$ vibrational mode of the acac ligand around 1520 cm^{-1} in the *tetrakis* Tm^{3+} complexes is in agreement with acac acting as the chelate ligand [8,24]. The absence of broadened absorption bands around 3500 cm^{-1} confirms that the compounds are anhydrous. The absorption peaks at 434, 427 and 424 cm^{-1} were assigned to the $Tm^{3+}\text{--O}$

vibrations in the complexes with Li^+ , Na^+ and K^+ counteranions, respectively [8,24]. The infrared absorption spectral profiles of the 3 *tetrakis* complexes are very similar, indicating that the acetylacetonato anion is coordinated to the rare earth ion.

The thermogravimetric curves (TG) (figure not shown) of $(\text{C})[\text{Tm}(\text{acac})_4]$ complexes with Li^+ , Na^+ and K^+ counteranions showed no mass loss in the range of 80–200 °C. These results indicate the absence of water molecules in these systems, indicating that these coordination compounds are anhydrous, corroborating with the infrared data.

Based on the X-ray diffraction patterns (Fig. 2), the three thulium complexes present high crystallinity. However, the data show that they are not isomorphous. This observation can be attributed to the different ionic radii of the alkali ions (Li^+ , Na^+ and K^+), which induce different environments around $[\text{Tm}(\text{acac})_4]^-$.

Fig. 3 shows the absorption spectra of the $(\text{C})[\text{Tm}(\text{acac})_4]$ complexes recorded in the near-infrared spectral range from 710 to 2100 nm, at room temperature. These spectra consist of narrow absorption bands arising from intraconfigurational 4f–4f transitions assigned to the ${}^3\text{H}_6 \rightarrow {}^3\text{F}_4$ (1725 nm), ${}^3\text{H}_6 \rightarrow {}^3\text{H}_5$ (1215 nm) and ${}^3\text{H}_6 \rightarrow {}^3\text{H}_4$ (799 nm) energy levels from the Tm^{3+} ion. The absorption spectral profiles for the Tm^{3+} -complexes are similar for the different alkaline metal ions. The barycenter of the observed ligand field components of each energy level presents red-shift when compared to the same 4f–4f transitions recorded for the $\text{Tm}^{3+}:\text{LaF}_3$ crystal matrix: ${}^3\text{H}_6 \rightarrow {}^3\text{F}_4$ (1707 nm), ${}^3\text{H}_6 \rightarrow {}^3\text{H}_5$

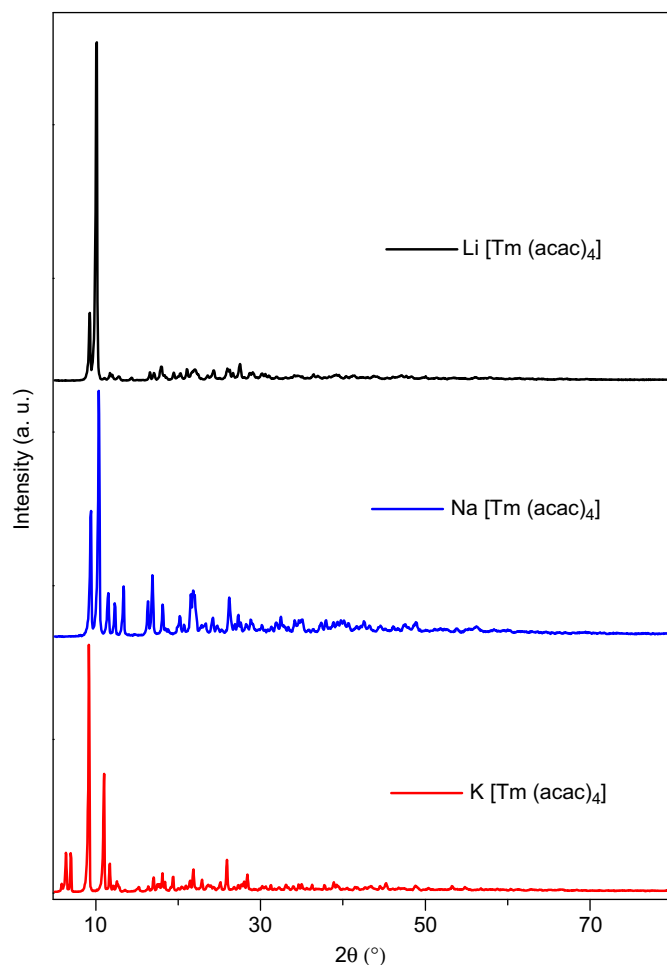


Fig. 2. X-rays powder diffraction patterns of the $(\text{C})[\text{Tm}(\text{acac})_4]$ complexes with $\text{C}^+ = \text{Li}^+$, Na^+ and K^+ counteranions.

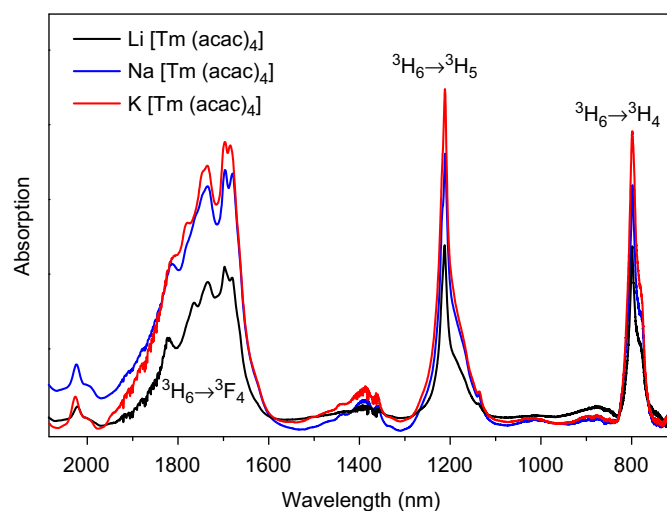


Fig. 3. Near-infrared absorption spectra of $(\text{C})[\text{Tm}(\text{acac})_4]$ complexes ($\text{C}^+ = \text{Li}^+$, Na^+ and K^+) at room temperature (298 K).

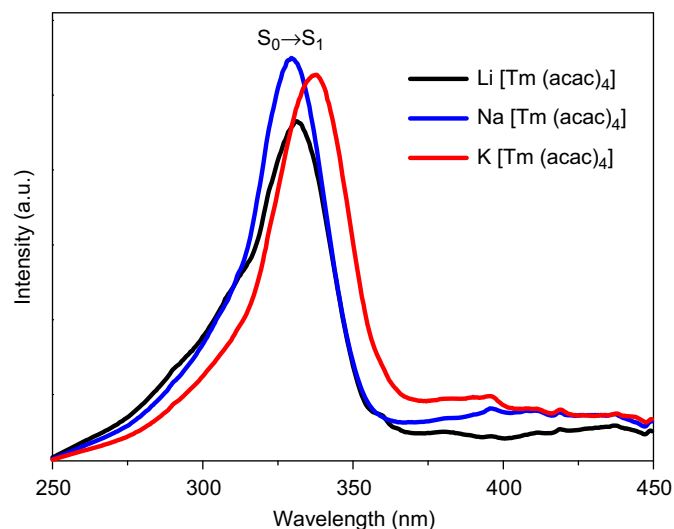


Fig. 4. Excitation spectra of $(\text{C})[\text{Tm}(\text{acac})_4]$ complexes ($\text{C}^+ = \text{Li}^+$, Na^+ and K^+) recorded at room temperature (298 K) on emission at 479 nm.

(1202 nm) and ${}^3\text{H}_6 \rightarrow {}^3\text{H}_4$ (787 nm) [25,26], showing clearly the *nephelauxetic* effect [27].

Fig. 4 presents the excitation spectra of the $(\text{C})[\text{Tm}(\text{acac})_4]$ complexes with $\text{C}^+ = \text{Li}^+$, Na^+ and K^+ recorded at ~ 298 K in the range 250–450 nm, under emission at 479 nm. These spectra present a strong broad band between 250 and 360 nm assigned to the photoexcitation process of the Tm^{3+} ion via absorption to the lower energy singlet excited states of the acac ligand. On the other hand, narrow bands corresponding to the intraconfigurational transitions of Tm^{3+} ion are not observed. This result shows that thulium luminescence sensitization through intramolecular energy transfer from the acac ligand to the Tm^{3+} ion is very efficient.

Emission spectra of the Tm^{3+} complexes in solid state, recorded in the range from 450 to 830 nm, under excitation on the acac ligand bands at ~ 325 nm, using a He–Cd laser, at 298 K, are shown in Fig. 5. The luminescence spectra show the characteristic ${}^1\text{G}_4 \rightarrow {}^3\text{H}_6$ (479 nm), ${}^1\text{G}_4 \rightarrow {}^3\text{F}_4$ (650 nm) and ${}^1\text{G}_4 \rightarrow {}^3\text{H}_5$ (779 nm) transitions of the Tm^{3+} ion, with the blue emission color at 479 nm as the most prominent one (Fig. 5). The emission spectra of the *tetrakis* complexes recorded at low

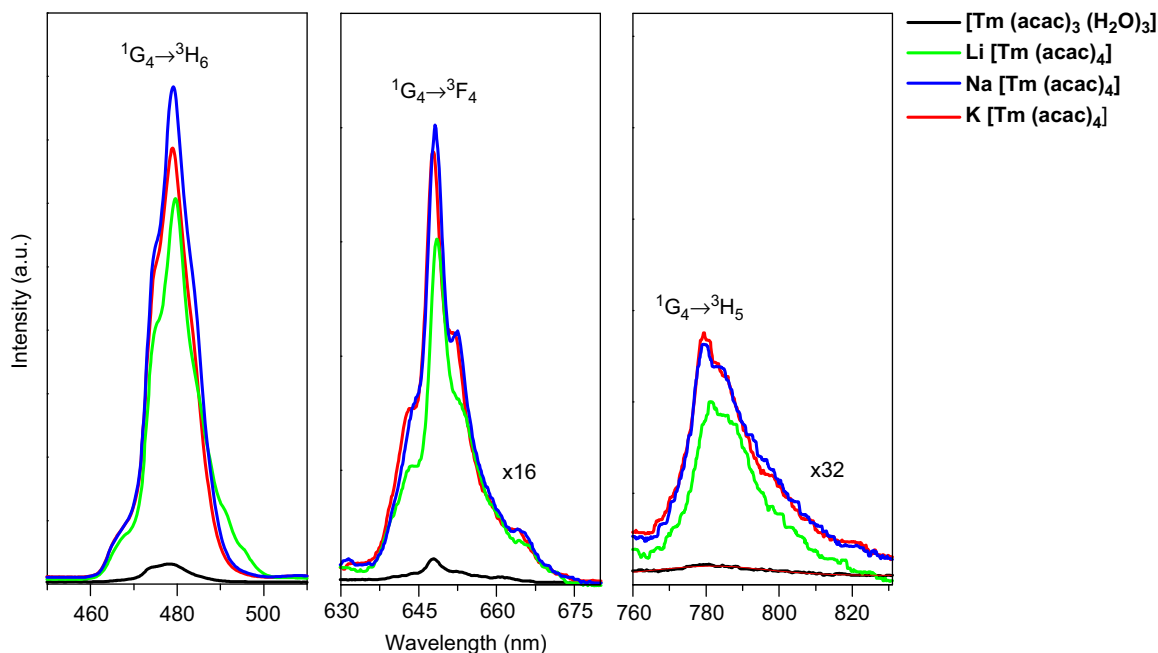


Fig. 5. Emission spectra of $[\text{Tm}(\text{acac})_3(\text{H}_2\text{O})_3]$ and $\text{C}[\text{Tm}(\text{acac})_4]$ complexes ($\text{C}^+ = \text{Li}^+, \text{Na}^+$ and K^+) recorded at room temperature (298 K) on excitation at 325 nm.

temperature (15 K) show the same spectral profiles as those obtained at 298 K, but they are 5 times more intense. The spectra (low and room temperature) are similar, with the low temperature one being better resolved. However, in both cases the acac ligand phosphorescence is not observed, indicating efficient energy transfer to the Tm^{3+} ion. The emission intensities in the *tetrakis* $\text{C}[\text{Tm}(\text{acac})_4]$ complexes are 20 times stronger than those in the *tris* $[\text{Tm}(\text{acac})_3(\text{H}_2\text{O})_3]$ complex (Fig. 5). This increase in luminescence intensity is due to the hindrance from water molecules in the first coordination sphere in the *tetrakis*-complexes.

The intramolecular energy transfer in the *tetrakis* RE^{3+} complexes from the β -diketonate ligands to RE^{3+} ions depends on the ligand's nature and the local symmetry of the metal ion [28,29]. In the $\text{C}[\text{Tm}(\text{acac})_4]$ complexes, the effect produced by changing the counteranion C^+ is clearly noted in both absorption and emission spectra.

From the luminescence decay curves (Fig. 6) we have determined the lifetime values (τ) of the emitting $^1\text{G}_4$ level at room temperature with a laser YAG:Nd, on excitation at 355 nm for 10 ns. These curves were fitted with a mono-exponential curve with lifetime values of 344, 360 and 400 ns for the Tm^{3+} - complexes with Li^+ , Na^+ and K^+ counteranions, respectively. An increasing linear behavior is observed when a graph of the lifetime vs. ionic radius of alkaline earth metal is plotted (inset Fig. 6), suggesting that the higher counteranion radius favors an emission quantum efficiency of the $^1\text{G}_4$ emitting level due to less operative non-radiative processes.

Besides, another feature in the photoluminescence emission data of the *tetrakis* complexes is that the emission spectra of all thulium acetylacetonato complexes do not exhibit the broad band of the acac ligands (Fig. 5). These optical data indicate an efficient intramolecular energy transfer from the triplet state of the acac ligand to the $^1\text{G}_4$ emitting energy level (Fig. 7a).

The $\text{C}[\text{Tm}(\text{acac})_4]$ complexes, by changing the counteranion $\text{C}^+ = \text{Li}^+, \text{Na}^+$ and K^+ , present similar (x,y) color coordinates (0.175, 0.203), (0.197, 0.222) and (0.190, 0.206), respectively, in the blue region of the CIE chromaticity diagram (Commission Internationale de l'Eclairage) (Fig. 7b) [30]. These three complexes

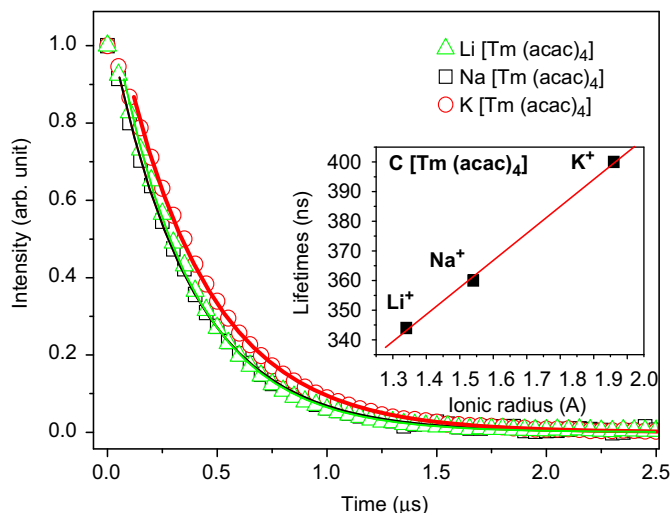


Fig. 6. Decay luminescence curves of $\text{C}[\text{Tm}(\text{acac})_4]$ complexes ($\text{C}^+ = \text{Li}^+, \text{Na}^+$ and K^+) recorded at room temperature (298 K) monitored with excitation at 355 nm and emission at 477 nm. Inset figure presents a plot of lifetimes (ns) vs. ionic radius (Å) of the complexes.

present emission blue color, indicating that these coordination compounds may act as efficient light conversion molecular devices (LCMDs) [31].

4. Conclusion

In summary, we have successfully prepared *tetrakis* Tm^{3+} complexes with an easy one-step synthesis. These compounds $\text{C}[\text{Tm}(\text{acac})_4]$ present intense narrow emission band in the blue region (centered at 480 nm) at room temperature, and are chemically stable and anhydrous. These data show that they can be used as efficient blue-component in full-color systems. Our future research will focus on the optimization of intramolecular energy transfer processes in these *tetrakis* systems by

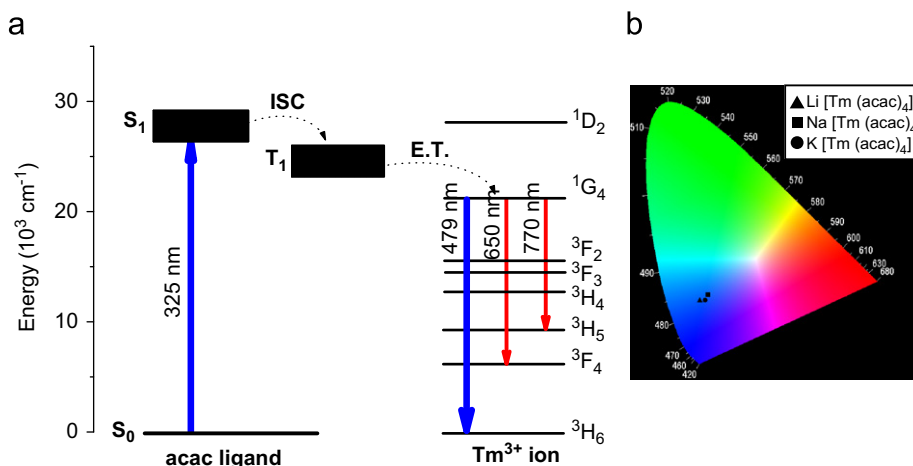


Fig. 7. (a) Partial energy level diagram of Tm^{3+} . Singlet and triplet states of acac ligand are shown on the left and arrows indicate emitting levels, where ISC=intersystem crossing and ET=energy transfer. (b) Chromaticity coordinates from emission spectra of the $\text{C}[\text{Tm}(\text{acac})_4]$ complexes.

tailoring the C^+ counterion in order to achieve pure emission color with high quantum yield, and ultimately the fabrication of emitting devices.

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References

- [1] S.V. Eliseeva, J.C.G. Bunzli, *Chem. Soc. Rev.* 39 (2010) 189.
- [2] I.A. Hemmilä, in: *Application of Fluorescence in Immunoassays*, Wiley, New York, 1991.
- [3] J. Kido, Y. Okamoto, *Chem. Rev.* 102 (2002) 2357.
- [4] L.M. Sweeting, *J. Am. Chem. Soc.* 109 (1987) 2652.
- [5] J. Kai, D.F. Parra, H.F. Brito, *J. Mater. Chem.* 18 (2008) 4549.
- [6] S.P. Sinha, in: *Europium*, Springer-Verlag, New York, 1967.
- [7] G.F. de Sá, O.L. Malta, C.D. Donega, A.M. Simas, R.L. Longo, P.A. Santa-Cruz, E.F. Silva, *Coord. Chem. Rev.* 196 (2000) 165.
- [8] K. Binnemans, in: K.A. Gschneidner Jr, J.C.G. Bunzli, V.K. Pecharsk (Eds.), *Handbook on the Physics and Chemistry of Rare Earths*, vol. 35, Rare-Earth Beta-Diketonates, Elsevier, Amsterdam, 2004, pp. 107–272.
- [9] H.F. Brito, O.L. Malta, M.C.F.C. Felinto, E.E.S. Teotonio, *The chemistry of metal enolates*, in: J. Zabicky (Ed.), *Luminescence Phenomena Involving Metal Enolates*, vol.1, John Wiley & Sons Ltd., England, 2009, pp. 131–184 Chapter 3.
- [10] O.L. Malta, H.F. Brito, J.F.S. Menezes, F.R. Gonçalves e Silva, S. Alves Jr, F.S. Farias, A.V.M. Andrade, *J. Lumin.* 75 (1997) 255.
- [11] F.S. Richardson, *Chem. Rev.* 82 (1982) 541.
- [12] E.E.S. Teotonio, M.C.F.C. Felinto, H.F. Brito, O.L. Malta, A.C. Trindade, R. Najjar, W. Streck, *Inorg. Chim. Acta* 357 (2004) 451.
- [13] A.J. Steckl, J. Heikenfeld, D.S. Lee, M. Garter, *Mater. Sci. Eng. B* 81 (2001) 97.
- [14] J. Feng, H.J. Zhang a, S.Y. Song, Z.F. Li, L.N. Sun, Y. Xing, X.M. Guo, *J. Lumin.* 128 (2008) 1957.
- [15] L.D. Carlos, Y. Messaddeq, H.F. Brito, R.A.S. Ferreira, V. de Zea Bermudez, S.J.L. Ribeiro, *Adv. Mater.* 12 (2000) 594.
- [16] J.B. Gruber, M.D. Seltzer, M.E. Hills, S.B. Stevens, C.A. Morrison, *J. Appl. Phys.* 73 (1993) 1929.
- [17] J. Holsa, R.J. Lamminm, E. Antic-Fidancev, M.L. Blaise, P. Porcher, *J. Phys.: Condens. Matter* 7 (1995) 5127.
- [18] W.R. Romanowski, S. Golabi, I. Sokólska, G.D. Dzik, J. Zawadzka, M. Berkowski, J.F. Finowicki, M. Baba, *Appl. Phys. B* 68 (1999) 199.
- [19] I. Sokólska, W. Ryba-Romanowski, S. Golab, M. Baba, M. Swirkowicz, T. Łukasiewicz, *J. Phys. Chem. Solids* 61 (2000) 1573.
- [20] U. Hömmerich, E.E. Nyein, D.S. Lee, A.J. Steckl, J.M. Zavada, *Appl. Phys. Lett.* 83 (2003) 4556.
- [21] P.R. Diamente, M. Raudsepp, F.C.J.M. van Veggel, *Adv. Funct. Mater.* 17 (2007) 363.
- [22] Y.D. Glinka, J.V. Foreman, H.O. Everitt, D.S. Lee, A.J. Steckl, *J. Appl. Phys.* 105 (2009) 083509-1.
- [23] S.M. Bruno, R.A.S. Ferreira, F.A. Almeida Paz, L.D. Carlos, M. Pillinger, P. Ribeiro-Claro, I.S. Gonçalves, *Inorg. Chim. Acta* 48 (2009) 4882.
- [24] K. Nakamoto, in: *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley & Sons, New York, 1997.
- [25] W.T. Carnall, P.R. Fields, J. Morrison, R. Sarup, *J. Chem. Phys.* 52 (1970) 4054.
- [26] W.T. Carnall, G.L. Goodman, K. Rajnak, R.S. Rana, A systematic analysis of the spectra of the lanthanides doped into single crystal LaF_3 . Argonne National Laboratory Report, ANL 88/08, 1988.
- [27] C.K. Jorgensen, in: *Modern Aspects of Ligand Field Theory*, North Holland Pub. Co., Amsterdam, 1971.
- [28] A. Mecha, M. Karbowiak, C. Görrler-Walrand, R.V. Deun, *J. Alloys Compd.* 451 (2008) 215.
- [29] K. Lunstroot, K. Driesen, P. Nockemann, C. Görrler-Walrand, K. Binnemans, S. Bellayer, J. Le Bideau, A. Vioux, *Chem. Mater.* 18 (2006) 5711.
- [30] N. Sabbatini, M. Guardigli, J.M. Lehn, *Coord. Chem. Rev.* 123 (1993) 201.
- [31] P.A. Santa-Cruz, F.S. Teles, *Spectra Lux Software v.2.0 Beta*, Ponto Quântico Nanodispositivos, RENAMI, 2003.