JOURNAL OF
Materials
CHEMISTRY

A comparative study on the electroluminescence properties of some terbium β-diketonate complexes

Youxuan Zheng, Jun Lin, Yujun Liang, Qin Lin, Yingning Yu, Qingguo Meng, Yonghui Zhou, Shubin Wang, Hongyan Wang and Hongjie Zhang*

Key Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry Chinese Academy of Sciences, Changchun 130022, People's Republic of China. E-mail: zhgroup@ns.ciac.jl.cn; zhhj@ns.ciac.ac.cn

Received 16th January 2001, Accepted 6th June 2001
First published as an Advance Article on the web 22nd August 2001

By comparing the phosphorescence spectra of Gd(acac)$_3$ (acac = acetylacetone), Gd(TFacac)$_3$ (TFacac = 1,1,1-trifluoroacetylacetone), the effects of fluorine replacement of hydrogen on the triplet state energy of the ligands were revealed. Fluorine can lower the triplet state energy of Hacac and make it more suitable for energy transfer towards the $^5D_4$ state of terbium. Organic electroluminescent devices (OELDs) with the corresponding trivalent terbium complexes as emissive layers were fabricated. Triple-layer-type devices with a structure of glass substrate/ITO (indium tin oxide)/PVK [poly(*N*-vinylcarbazole)]/PVK : Tb complex: PBD [2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole]/PBD/Al exhibit bright green luminescence upon applying a dc voltage. The luminance of a device with Tb(TFacac)$_3$phen (1,10-phenanthroline) and Tb(TFacac)$_3$ as emissive layer is higher than that of the corresponding devices with Tb(acac)$_3$(phen) and Tb(acac)$_3$ as emissive layers. The EL device with Tb(TFacac)$_3$(phen) as emitter exhibits characteristic emission of Tb^{3+} ions with a maximum luminance of 58 cd m^{-2} at 25 V.

Introduction

Organic electroluminescent devices (OELDs) based on organic thin film layers are one of the most promising next-generation flat panel full color display systems. Since the pioneering work of Tang and VanSlyke[1] on organic electroluminescent devices with double layers and the original report of polymer EL from a precursor-route poly(*p*-phenylenevinylene) (prec-PPV) by Burroughes *et al.*,[2] the field of OEL has rapidly established itself as a new branch of applied science. A variety of organic materials, including fluorescent dyes,[3,4] metal complexes[5] and polymers,[6–13] have been reported to show electroluminescence, and various emission colors have been obtained. However, these OELDs using organic materials and polymers as the emissive layers generally produce emission due to their π–π* transition, whose luminescence spectra typically have a large full width at half maximum (50–200 nm) and are not well suited for actual multicolor display applications.

Besides these organic molecules, another type of promising compounds, rare earth complexes, are anticipated to exhibit narrow emission spectra along with high efficiency. The rare earth ions exhibit sharp spectral bands corresponding to f–f electron transitions. In the past decades, many rare earth complexes, especially those containing terbium and europium, have been used in OELDs as the emissive materials.[14–32] Most of the work was focused on rare earth β-diketonate complexes because of their good solubility and/or good volatility. Among those the terbium β-diketonate complex Tb(acac)$_3$ was first introduced into OELDs by Kido *et al.*,[14] and later Tb(acac)$_3$(phen) was used as an emissive center and the performance of the OELDs was improved.[33]

Our group has been concentrating on the investigation of the photoluminescent (PL) and electroluminescent (EL) properties of rare earth complexes.[16,19,34] In order to enhance the solubility of the rare earth carboxylate complexes in organic solvents, we introduced a long alkyl chain to the ligands and fabricated several EL devices.[16,17,19,20] Additionally, we have observed a 1.5 μm infrared emission in an EL device using an erbium organic complex as the emissive layer.[31]

In the present paper, we prepared four Tb^{3+} complexes, *i.e.* Tb(acac)$_3$, Tb(TFacac)$_3$, Tb(acac)$_3$(phen) and Tb(TFacac)$_3$(phen), and studied their photoluminescent and electroluminescent properties to allow comparison. Gd(acac)$_3$ and Gd(TFacac)$_3$ were also prepared to allow determination of the triplet state energy of the ligands. It is observed that the triplet state energy of the Hacac decreases when hydrogen is replaced by fluorine within the Hacac ligand. This is more suitable for energy transfer towards the $^5D_4$ state of Tb^{3+}, resulting in an improvement of the emission intensity of Tb^{3+}.

Experimental

Materials

Terbium oxide (Tb_4O_7, 99.99%) and gadolinium oxide (Gd_2O_3, 99.9%) were purchased from Yue Long Chemical Plant (Shanghai, China). Acetylacetone (Hacac, 98.0%) and 1,1,1-trifluoroacetylacetone (HTFacac, 98.0%) were obtained from Aldrich (USA). Hydrochloric acid (HCl, 37%, A. R.) and 1,10-phenanthroline (phen, 99.0%, A. R.) were purchased from Beijing Chemical Company (Beijing, China). Indium tin oxide (ITO) coated glass substrates were purchased from Guang Ming Glass Company (Shenzhen, China).

Synthesis of the rare earth complexes

$TbCl_3$ and $GdCl_3$ ethanol solutions were prepared as follows: the rare earth oxide (Tb_4O_7, Gd_2O_3) was dissolved in concentrated hydrochloric acid and the surplus HCl removed by evaporation. The residue was diluted with 95% ethanol. The concentration of the rare earth ion was measured by titration with a standard EDTA (ethylenediaminetetraacetic acid) aqueous solution.

The six rare earth complexes were synthesized by conventional methods.[35]

DOI: 10.1039/b100558h

(1) Binary complexes: 1 mmol $TbCl_3$ or $GdCl_3$ ethanol solution was added dropwise to a solution of 3 mmol β-diketone in ethanol which had been neutralized with 3 mmol NaOH aqueous solution beforehand and stirred under heating.

(2) Ternary complexes: 1 mmol $TbCl_3$ ethanol solution was added dropwise to a mixed solution of 3 mmol β-diketone and 1 mmol phen in ethanol which had also been neutralized with 3 mmol NaOH aqueous solution beforehand and stirred under heating.

Then, the mixtures were stirred at 60 °C for 5 h and white precipitates were obtained. The precipitates were filtered off and washed with ethanol, deionized water and ethanol and purified by reprecipitation from hexane, and finally dried *in vacuo* at 80 °C for 48 h. The results of elemental analysis for the four terbium complexes are given in Table 1.

Preparation of the EL devices

Four EL devices with $Tb(TFacac)_3(phen)$ (denoted as ELa), $Tb(acac)_3(phen)$ (ELb), $Tb(TFacac)_3$ (ELc) and $Tb(acac)_3$ (ELd) as emissive layers, were fabricated and their different electroluminescent properties were compared. Fig. 1 shows the device configuration and the molecular structures of the materials used in this study. The devices were fabricated on glass substrates coated with a patterned ITO with a sheet resistance of $70\ \Omega\ \square^{-1}$ which were etched to form strips of 2 mm width and were used as anodes. The substrates were ultrasonically cleaned in toluene, acetone and ethanol, and then rinsed with deionized water. After drying under an infrared lamp, the substrates were coated with the hole-transporting layer PVK [poly(*N*-vinylcarbazole)] by a spin-coating process (the coating solution was prepared by dissolving 10 mg PVK in 1 ml chloroform). PVK is widely used in many studies because of its good hole-transporting and film-forming properties. The terbium complexes were blended with the PVK and an electron-transporting material PBD [2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole] because of their poor film-forming and carrier-transporting ability. In addition, this can also prevent the self-quenching of the luminescence of the terbium complex.[21] Thus, the injection of electrons and holes in the emissive layer will be greatly enhanced and a good film can be obtained by the spin-casting process. This method not only simplifies the fabrication process, but also avoids thermal decomposition of luminescent materials caused by evaporation under vacuum. The weight ratio of PVK : PBD : Tb complex is 10 : 8 : 2 (mg) in 1 ml chloroform. The spinning speed used was 1500 rpm and the two layers were coated two times, each time for 20 s. Then, another layer of PBD (100 nm) was deposited by vacuum evaporation on the emissive layer as the electron-injection layer in a chamber at a pressure of $<1\times10^{-3}$ Pa. Finally, an electron injection Al electrode (1000 nm) was deposited on top by vacuum evaporation. The deposition rates were 0.5 nm s^{-1} for PBD and 2 nm s^{-1} for Al.

Measurements

The elemental analysis of the four Tb^{3+}-complexes was carried out with an Elementar Analysensysteme GmbH VarioEL. The low temperature phosphorescence spectra of Gd^{3+}-complexes were measured on a SPEX1934D spectrophotometer using a 7 W xenon lamp as the excitation source at liquid nitrogen temperature (77 K). The photoluminescent (PL, excitation and emission) and electroluminescence (EL) spectra were measured with a SPEX FL-2T2 and a Shimadzu RF5000 spectrofluorophotometer, respectively. The current–bias voltage and luminance–bias voltage curves were obtained on a KEITHLEY2400 Sourcemeter.

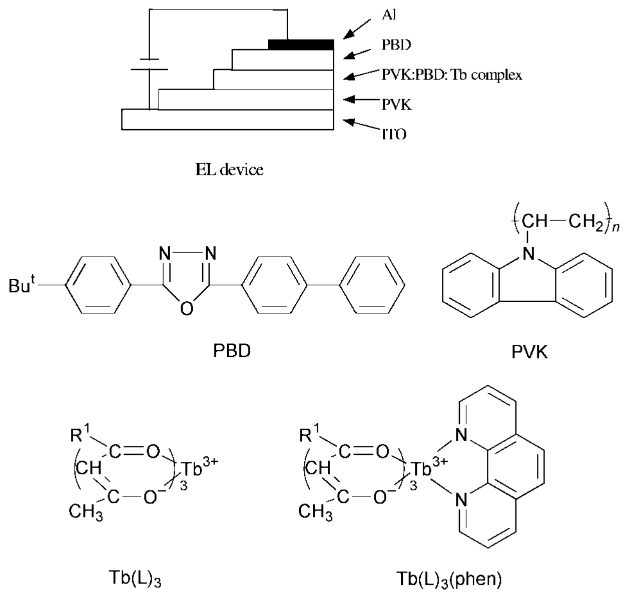

Fig. 1 The configuration of the EL devices and molecular structures of materials used (L = acac, $R^1 = CH_3$; L = TFacac, $R^1 = CF_3$).

Results and discussion

For a better understanding of the optical properties of these complexes, comparative investigations were carried out under the same conditions.

The excitation spectra of the four Tb^{3+}-complexes by monitoring the Tb^{3+} emission at 548 nm are shown in Fig. 2. It can be observed that all the spectra show a maximum peak at 328 nm with two shoulders at 358 and 378 nm. The former is due to the absorption of the ligands, and the latter (two shoulders) is due to the f–f electron transitions of Tb^{3+}. The sequence of the excitation intensity of the four complexes is I $[Tb(TFacac)_3(phen)] > I$ $[Tb(acac)_3(phen)] > I$ $[Tb(TFacac)_3] > I$ $[Tb(acac)_3]$.

Excitation into the ligand at 328 nm yields bright green emission. Fig. 3 shows emission spectra of the four complexes. From Fig. 3 it can be seen that the emission spectra consist of the characteristic transition lines of Tb^{3+} at 487 nm ($^5D_4 \rightarrow {}^7F_6$), 543 nm ($^5D_4 \rightarrow {}^7F_5$), 583 nm ($^5D_4 \rightarrow {}^7F_4$) and 621 nm ($^5D_4 \rightarrow {}^7F_3$). No emission from the ligands of the complexes is observed. This indicates that a very efficient energy transfer occurs from the ligand to the central Tb^{3+}. Similarly to the sequence of the excitation intensity, the emission intensity of the four Tb^{3+}-complexes also changes

Table 1 The results of elemental analysis of the four terbium complexes

	Found (%)				Calculated (%)			
	C	H	O	N	C	H	O	N
$Tb(acac)_3$	39.42	4.65	21.05	—	39.49	4.64	21.04	—
$Tb(TFacac)_3$	29.13	1.97	15.55	—	29.15	1.96	15.53	—
$Tb(acac)_3(phen)$	50.94	4.60	15.10	4.41	50.95	4.59	15.08	4.40
$Tb(TFacac)_3(phen)$	40.61	2.54	12.03	3.51	40.62	2.53	12.02	3.51

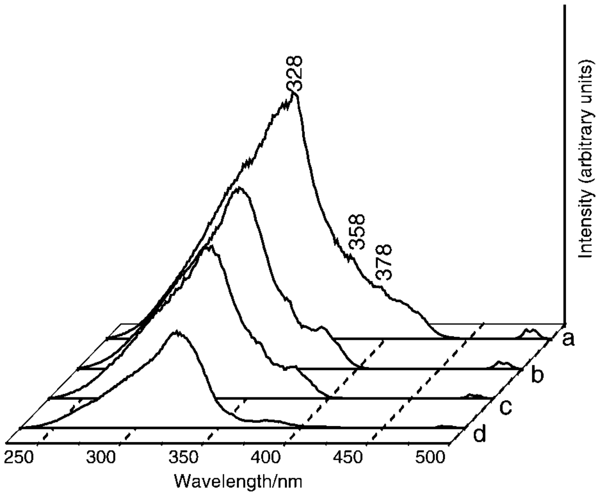

Fig. 2 The excitation spectra of the four terbium complexes (λ_{em} = 543 nm). a: Tb(TFacac)$_3$(phen), b: Tb(acac)$_3$(phen), c: Tb(TFacac)$_3$, d: Tb(acac)$_3$.

as I [Tb(TFacac)$_3$(phen)] > I [Tb(acac)$_3$(phen)] > I [Tb(TFacac)$_3$] > I [Tb(acac)$_3$]. These results suggest that both the introduction of fluorine in the Hacac ligand and the introduction of the third ligand phen are able to enhance the efficiency of energy transfer from the ligands to the central Tb^{3+}, resulting in the improvement of its emission intensity.

In order to determine the triplet energy state of Hacac and HTFacac, the low temperature phosphorescence spectra of the Gd(acac)$_3$ and Gd(TFacac)$_3$ complexes (5×10^{-4} M chloroform CHCl$_3$ solution) were measured at 77 K. The lowest excitation state of Gd^{3+} (^{6}P) is located at about 32000 cm^{-1}, which is much higher than the energy of the triplet state of ligands, therefore energy transfer from the ligands to Gd^{3+} is impossible. Thus the phosphorescence spectra of Gd(acac)$_3$ and Gd(TFacac)$_3$ are due to the emission of the ligands, and the emission band at the shortest wavelength is assumed to be a 0–0 transition (from the lowest triplet energy state to the ground state of the ligand). In this way the lowest energy of the triplet state of the ligand can be determined.

Fig. 4 shows the phosphorescence spectra of the ligands of complexes Gd(acac)$_3$ and Gd(TFacac)$_3$. In this figure, it can be observed that phosphorescence in Gd(TFacac)$_3$ shifts to lower energy relative to that of Gd(acac)$_3$ (from 395 nm for the latter to 440 nm for the former). Because fluorine is heavier than hydrogen, the vibration energy of the C–F bond (ν = 1350–1120 cm^{-1}) is lower than that of the C–H bond (ν = 2800–3000 cm^{-1}).[36] The excitation energy loss due to the C–F vibration in HTFacac is lower than that in Hacac due to the C–H vibration. Table 2 lists the lowest triplet state energies of Hacac, HTFacac and the energy differences between the ligands and Tb^{3+} ion (^{5}D$_4$ = 20500 cm^{-1}).

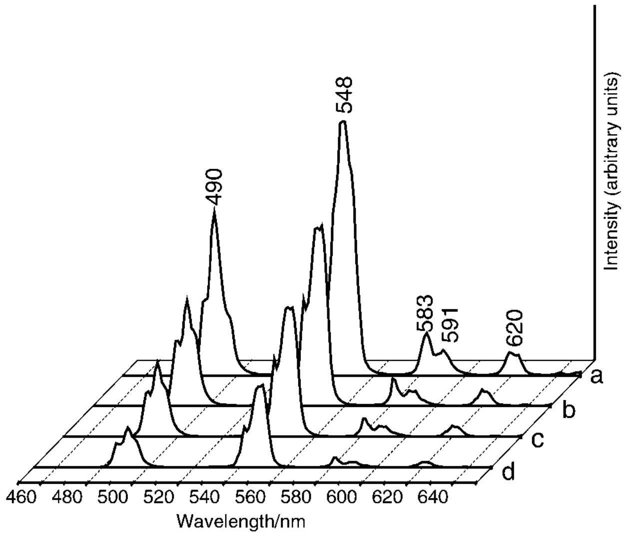

Fig. 3 The emission spectra of the four terbium complexes (λ_{ex} = 328 nm). a: Tb(TFacac)$_3$(phen), b: Tb(acac)$_3$(phen), c: Tb(TFacac)$_3$, d: Tb(acac)$_3$.

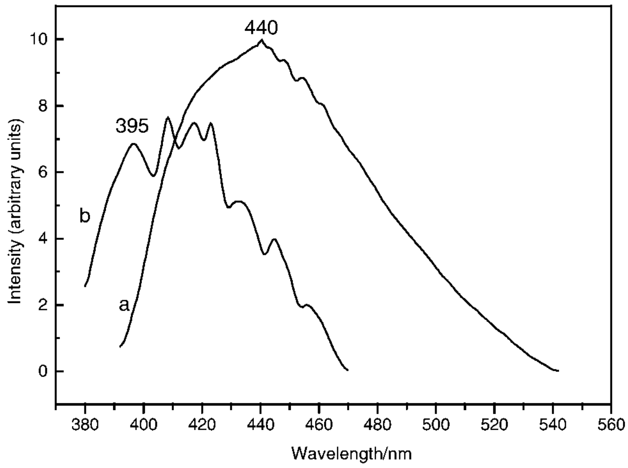

Fig. 4 The phosphorescence spectra of a: Gd(TFacac)$_3$ (λ_{ex} = 354 nm) and b: Gd(acac)$_3$ (λ_{ex} = 302 nm) complexes in CHCl$_3$ (5×10^{-4} M).

Generally, the fluorescence of lanthanide metal complexes is generated by an excitation energy transfer from the ligand to the central metal ion in the excited state. In this case, the excitation energy of the ligand is transferred to the central ion through the ligand's triplet energy level. The energy difference between the triplet state energy of the organic ligand (Tr) and the resonant emitting level of ^{5}D$_4$ of the Tb^{3+} ion can be calculated [ΔE(Tr–^{5}D$_4$)] (see Table 2). According to Sato and Wada, the intramolecular energy migration efficiency from organic ligands to the central Ln^{3+} is the most important factor influencing the luminescence properties of rare earth complexes.[37] The larger is ΔE(Tr–Tb^{3+}) the lower is the luminescence efficiency of the rare earth complexes.[38]

The luminescence theory of rare earth organic complexes indicates that when ΔE(Tr–^{5}D$_4$) is 2400 ± 300 cm^{-1}, organic ligands can efficiently sensitize Tb^{3+} ion fluorescence.[37] Here ΔE(Tr–^{5}D$_4$) between HTFacac and Tb^{3+} ion is 2220 cm^{-1} while the corresponding difference between Hacac and Tb^{3+} ion is 4810 cm^{-1}. Therefore the luminescence intensity of the Tb–TFacac complexes is stronger than that of the Tb–acac complex. The introduction of phen can enhance the luminescence intensity of Tb^{3+} in Tb^{3+}–β-diketone complexes. This is due to the intramolecular energy transfer from β-diketone to phen, then from phen to Tb^{3+} because the triplet state energy of β-diketone is much higher than that of phen.[39] According to Rohatgi,[40] phen is also a synergic agent, which not only saturates the coordination number of the terbium ion, but also shields against the influence of water molecules. This leads the luminescence intensity of Tb(acac)$_3$(phen) to be stronger than that of Tb(TFacac)$_3$.

The EL spectra of the devices are shown in Fig. 5 at 12 V, related data of which are listed in Table 3. It can be seen that the EL spectra are similar to the PL emission spectra of the

Table 2 The lowest triplet state energies of acac, TFacac and the energy differences between the ligands and Tb^{3+} ion (^{5}D$_4$ = 20500 cm^{-1})

Ligand	Transition/nm	Triplet energy/cm^{-1}	ΔE(Tr–^{5}D$_4$)/cm^{-1}
Acac	395	25310	4810
TFacac	440	22720	2220

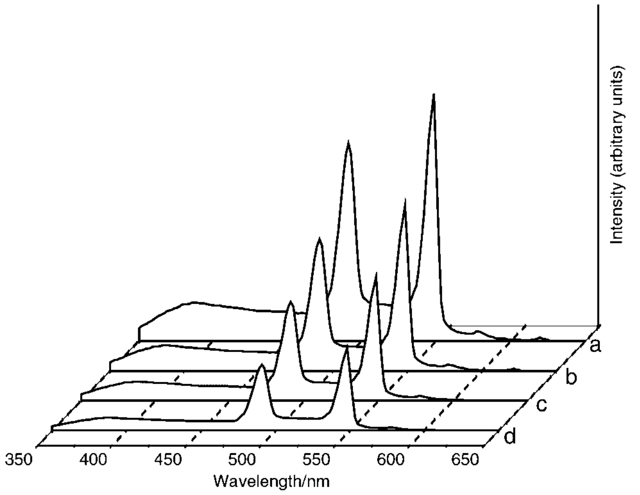

Fig. 5 The electroluminescence spectra of the four devices with the corresponding terbium complexes as emissive centers. a: Tb(TFacac)$_3$(phen), b: Tb(acac)$_3$(phen), c: Tb(TFacac)$_3$, d: Tb(acac)$_3$.

Table 3 Comparison of the four EL devices

	Luminance yield η (%)	Luminescence start voltage/V	Maximum luminance L/cd m^{-2}
ELa	0.25	8	58
ELb	0.16	10	36
ELc	0.11	11	25
ELd	0.08	13	17

complexes, demonstrating that the hole–electron recombination occurs in the terbium complex layer only. They also obey the strength sequence of photoluminescence, *i.e.*, I [Tb(TFacac)$_3$(phen)] > I [Tb(acac)$_3$(phen)] > I [Tb(TFacac)$_3$] > I [Tb(acac)$_3$]. The electroluminescence from the four devices shows weak emission of PBD with a maximum at 420 nm, which is responsible for the background signals in Fig. 5. As mentioned above, the central metal ion is excited through the excitation of the ligand in lanthanide metal complexes. In this case, the excited energy at the π conjugation of the ligand is transferred to the central ion through the ligand's triplet energy level.[21] Holes inject from ITO through PVK and electrons inject from Al through PBD to the PVK : PBD : Tb complex. The energy from the hole–electron recombination is transferred to the ligands and finally to the central Tb^{3+} ions. The energy transfer mechanism and emission mechanism for EL and PL are similar, and only the origins of the excitation energy are different. From the spectra we also find peaks at about 380–430 nm, which arise from the luminescence of PBD. PBD has electron transport properties,[41,42] but does not possess high hole-blocking properties.[43] It is therefore possible to inject holes into the PBD layer so leading to recombination of the carriers in this layer and thus luminescence of PBD is observed.

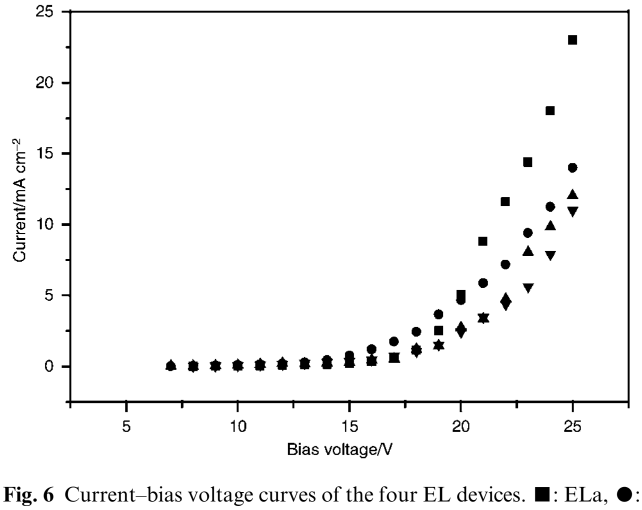

Fig. 6 Current–bias voltage curves of the four EL devices. ■: ELa, ●: ELb, ▲: ELc, ▼: ELd.

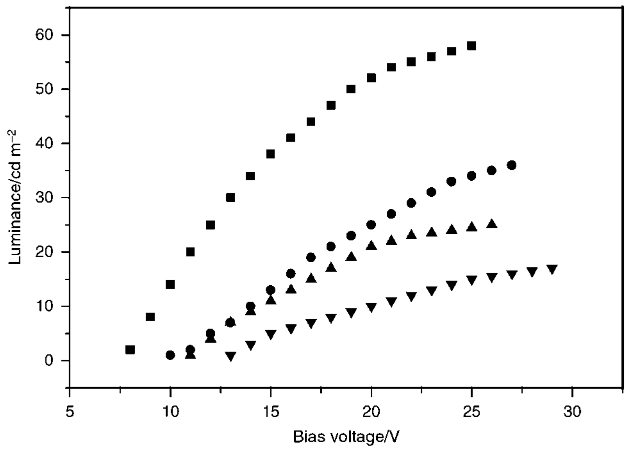

Fig. 7 The luminance–bias voltage curves of the four EL devices. ■: ELa, ●: ELb, ▲: ELc, ▼: ELd.

Current–bias voltage and luminance–bias voltage characteristics of the EL devices are shown in Fig. 6 and Fig. 7, respectively. Positive bias condition is defined as the case in which the ITO electrode is biased positively and the Al electrode negatively. All of the four devices have characteristics of a diode. From Table 3 it is seen that the luminescence of ELa starts at 8 V and the maximum luminance of 58 cd m^{-2} is achieved at 25 V, which is the best performance among the four devices. The higher EL luminance is due to the higher PL luminescence of the complex.

Conclusion

It can be concluded that the replacement of hydrogen by fluorine in the ligand Hacac lowers the vibration energy of the ligand, which decreases the energy loss caused by ligand vibration and enhances PL and EL emission intensity of Tb^{3+}. This is a novel approach to improve the properties of EL devices. We have succeeded in obtaining bright green electroluminescence through the use of Tb(TFacac)$_3$(phen) as the emissive center in a triple layered device. The maximum luminance of this device is 58 cd m^{-2} at 25 V.

Acknowledgements

We acknowledge financial aid from "973"—National Key Project for Fundamental Research of Rare Earth Functional Materials of China, National Natural Science Foundation of China (No.29731010, No.29971030) and "Barenjihua" of Chinese Academy of Science.

References

1 C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.*, 1987, **51**, 913.
2 J. H. Burroughes, D. D. C. Bradley, A. R. Brown, N. Marks, K. Mackay, R. H. Friend, P. L. Burns and A. B. Holmes, *Nature*, 1990, **347**, 539.
3 C. Adachi, S. Tokito, T. Tsutsui and S. Saito, *Jpn. J. Appl. Phys.*, 1988, **27**, 269.
4 J. Kido, C. Ohtaki, K. Hongawa, K. Okugama and K. Nagai, *Jpn. J. Appl. Phys.*, 1993, **32**, 917.
5 Y. Hamada, T. Sano, M. Fujita, T. Fujii, Y. Nishioma and K. Shibato, *Jpn. J. Appl. Phys.*, 1993, **32**, 514.
6 J. Kido, *Trends Polym. Sci.*, 1994, **10**, 350.
7 A. J. Epstein, Y. Z. Wang, S. W. Jessen, J. W. Blatchford,

D. D. Gebler, L. B. Lin, T. L. Gustafson, T. M. Swager and A. G. MacDiarmid, *Polym. Prep.*, 1996, **37**, 133.

8 H. L. Wang, A. G. MacDiarmid, Y. Z. Wang, D. D. Gebler and A. J. Epstein, *Synth. Met.*, 1996, **78**, 33.

9 Y. Z. Wang, D. D. Gebler, D. K. Fu, T. M. Swager and A. J. Epstein, *Appl. Phys. Lett.*, 1997, **70**, 3215.

10 Y. Z. Wang, R. G. Sun, F. Meghdadi, G. Leising, T. M. Swager and A. J. Epstein, *Synth. Met.*, 1999, **102**, 889.

11 Y. Z. Wang, R. G. Sun, T. M. Swager and A. J. Epstein, *Appl. Phys. Lett.*, 1999, **74**, 2593.

12 Y. Z. Wang, R. G. Sun, F. Meghdadi, G. Leising, T. M. Swager and A. J. Epstein, *Appl. Phys. Lett.*, 1999, **74**, 3613.

13 R. G. Sun, Y. Z. Wang, D. K. Wang, Q. B. Zheng, E. M. Kyllo, T. L. Gustafson and A. J. Epstein, *Appl. Phys. Lett.*, 2000, **76**, 634.

14 J. Kido, K. Nagai and Y. Ohashi, *Chem. Lett.*, 1990, **220**, 657.

15 A. Edwards, C. Claude, I. Sokolik, T. Y. Chu, Y. Okamoto and R. Dorsinvill, *J. Appl. Phys.*, 1997, **82**, 1841.

16 B. Li, D. G. Ma, H. J. Zhang, X. J. Zhao and J. Z. Ni, *Thin Solid Films*, 1998, **325**, 259.

17 D. G. Ma, D. K. Wang, B. Li, Z. Y. Hong, S. Lu, L. X. Wang, N. Minami, N. Takada, Y. Ichino, K. Yase, H. J. Zhang, X. B. Jing and F. S. Wang, *Synth. Met.*, 1999, **102**, 1136.

18 X. C. Gao, H. Cao, C. H. Huang, B. G. Li and S. Umitani, *Appl. Phys, Lett.*, 1998, **12**, 2217.

19 Y. X. Zheng, C. Y. Shi, Y. J. Liang, Q. Lin, C. Guo and H. J. Zhang, *Synth. Met.*, 2000, **14**, 321.

20 Q. Lin, C. Y. Shi, Y. J. Liang, Y. X. Zheng, S. B. Wang and H. J. Zhang, *Synth. Met.*, 2000, **14**, 373.

21 J. Kido, H. Hagase, K. Hongawa and K. Nagai, *Appl. Phys. Lett.*, 1994, **65**, 2124.

22 T. Sano, M. Fujita, T. Fujii, Y. Hamada, K. Shibata and K. Kuroki, *Jpn. J. Appl. Phys.*, 1995, **34**, 1883.

23 R. A. Campos, I. P. Kovaley, Y. Guo, N. Wakili and T. Skotheim, *J. Appl. Phys.*, 1996, **80**, 7144.

24 G. F. de Sá, S. A. Jr, B. J. P. Da Silva and E. F. da Silva Jr, *Opt. Mater.*, 1998, **11**, 23.

25 K. Okada, M. Uekawa, Y. F. Wang, T. M. Chen and T. Nakaya, *Chem. Lett.*, 1998, 801.

26 M. D. McGehee, T. Bergstedt, C. Zhang, A. P. Saab, M. B. O'Regan, G. C. Bazan, V. I. Srdanov and A. J. Heeger, *Adv. Mater.*, 1999, **11**, 1349.

27 K. Okada, Y. F. Wang, T. M. Chen, M. Kitamura, T. Nakaya and H. Inoue, *J. Mater. Chem.*, 1999, **9**, 3023.

28 G. Yu, Y. Q. Liu, X. Wu, D. B. Zhu, H. Y. Li, L. P. Jin and M. Z. Wang, *Chem. Mater.*, 2000, **12**, 2537.

29 M. Iwamuro, T. Adachi, Y. Wada, T. Kitamura and S. Yanagida, *Chem. Lett.*, 1999, 539.

30 O. M. Khreis, R. J. Curry, M. Somerton and W. P. Gillin, *J. Appl. Phys.*, 2000, **87**, 7589.

31 R. G. Sun, Y. Z. Wang, B. B. Zheng, H. J. Zhang and A. J. Epstein, *J. Appl. Phys.*, 2000, **87**, 7589.

32 Y. Kawamura, Y. Wada, M. Iwamura, T. Kitamura and S. Yanagida, *Chem. Lett.*, 2000, 280.

33 W. L. Li, J. Q. Yu, G. Sun, Z. R. Hong, Y. Yu, Y. Zhao, J. B. Peng and T. Tsutsui, *Synth. Met.*, 1997, **91**, 263.

34 B. Yan, H. J. Zhang, S. B. Wang and J. Z. Ni, *Mater. Chem. Phys.*, 1997, **51**, 92.

35 L. R. Melby, N. J. Rose, E. Abramson and J. C. Caris, *J. Am. Chem. Soc.*, 1964, **86**, 5117.

36 *Infrared Spectra Analysis and New Technology (in Chinese)*, ed. S. L. Zhang, D. N. Yi and T. M. Wu, Press of Science and Technology of Chinese Medicine, Beijing, 1993, p. 104.

37 S. Sato and M. Wada, *Jpn. Bull. Chem.*, 1970, **43**, 1955.

38 F. Deschryer and G. A. Crosby, *J. Mol. Spectrosc.*, 1962, **8**, 315.

39 B. Yan, H. J. Zhang, S. B. Wang and J. Z. Ni, *J. Photochem. Photobiol. A: Chem.*, 1998, **116**, 209.

40 K. K. Rohatgi, *J. Sci. Ind. Res.*, 1965, **24**, 456.

41 C. Adachi, T. Tsutsui and S. Saito, *Appl. Phys. Lett.*, 1989, **55**, 1489.

42 C. Adachi, T. Tsutsui and S. Saito, *Appl. Phys. Lett.*, 1990, **57**, 537.

43 J. Kido, C. Ohtaki, K. Hongawa, K. Okuyama and K. Nagai, *Jpn. J. Appl. Phys*, 1993, **32**, 2917.