

# Double Fluorescence Conversion in Ultraviolet and Visible Region for Some Praseodymium Complexes of Aromatic Carboxylates

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**Abstract** Four praseodymium complexes of aromatic carboxylates (benzoate, 4-tert-butylbenzoate, 2-benzoylbenzoate, and benzimidazole-5-carboxylate) have been synthesized and characterized, whose photophysical properties have been studied with ultraviolet spectra, phosphorescence spectra, and fluorescence spectra. The fluorescent emission spectra of all praseodymium complexes show two emission peaks under the excitation band of 245 nm at about 395 and 595 nm respectively, while one peak under 415 nm at about 595 nm, which attributed to be  $^1S_0 \rightarrow ^1I_6$  (395 nm) transition and the characteristic emission  $^1D_2 \rightarrow ^3H_4$  (595 nm) transition of  $Pr^{3+}$  ion. The  $^1S_0 \rightarrow ^1I_6$  transition can be ascribed as the transition of charge transfer state, and the  $^1D_2 \rightarrow ^3H_4$  can be further proved that there exists an antenna effect in the fluorescence of praseodymium with aromatic carboxylic acids. In conclusion, the praseodymium complexes systems can realize the double fluorescent conversion in both ultraviolet and visible region and can be further studied the application of this conversion.

**Keywords** Fluorescence conversion · Praseodymium complexes · Aromatic carboxylate · Molecular spectroscopy

## Introduction

The fluorescent properties of lanthanide coordination compounds with organic ligands have been the subject of great interest for these functional molecular systems have great potential applications as the active center of fluorescent ma-

terials and devices or as structural and functional probe, sensors or labels for the chemical and biological macromolecule systems [1–10]. There were a lot of reports on the fluorescence, energy match and energy transfer mechanism of lanthanide complexes with  $\beta$ -diketones, aromatic carboxylic acids and heterocyclic ligands, which show good energy coupling and, afterwards good fluorescent properties of lanthanide ions [11–13]. Beeby *et al.* have carried out a lot of research on the photophysical properties of lanthanide complexes with specially designed ligands [14–22]. We have reported the energy match and intramolecular energy transfer mechanism of binary and ternary lanthanide complexes with aromatic carboxylic acids and 1,10-phenanthroline in details [23–25]. To presence, the most general fluorescence mechanism is the intramolecular-energy transfer from the organic ligands to the lanthanide ions, which depends on the energy match between the triplet state energies of organic ligands and the resonant energy levels of trivalent lanthanide ions. Especially lanthanide complexes of aromatic carboxylates have higher thermal or fluorescent stabilities for practical applications than other lanthanide systems because they readily form polymeric structures [26–31]. Besides this, there exist some examples conforming to the different energy transfer process. Wang *et al.* [32] observed the directly energy transfer from the singlet-state energy of ligands to europium ions. Naturally, there also exist the fluorescence corresponded to the ligand— $Ln^{3+}$  charge transfer state which belongs to the feature of ligands, similar to some transition metal (Zn, etc.) complex systems [33]. It was found that most triplet-state energies of  $\beta$ -diketones are more suitable for the resonant energy level of  $Eu^{3+}$  and most  $Eu^{3+}$  complexes with  $\beta$ -diketones can show the strong emission of  $Eu^{3+}$  except for acetylactone [34]. While we discovered that most triplet-state energies of aromatic carboxylic acids are more suitable for the resonant energy level of  $Tb^{3+}$  and most  $Tb^{3+}$

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complexes with  $\beta$ -diketones can show the strong emission of  $\text{Tb}^{3+}$  [35]. Unfortunately, little attention has been paid on praseodymium complexes with organic ligands except that there exist some reports on the fluorescence of  $\text{Pr}^{3+}$  in some titanates or zirconates ceramics, which show the red emission to the  $^1\text{D}_2 \rightarrow ^3\text{H}_4$  transition of  $\text{Pr}^{3+}$  [36, 37]. Praseodymium ion exhibits abundant characteristic transitions and different systems exhibit different emission. Voloshin *et al.* [38] observed the luminescence of  $\text{Pr}^{3+}$  in both visible and infrared region in its chelates of some  $\beta$ -diketones or carboxylates. In the context, a series of twelve praseodymium complexes were synthesized and the corresponding photophysical properties were studied in detail. We found the luminescence of  $\text{Pr}^{3+}$  in UV–vis region for its aromatic carboxylates.

## Experimental

### Synthesis of lanthanide complexes

$\text{Pr}_6\text{O}_{11}$  was converted to its nitrate by treating with concentrated nitric acid together with some petroxide. Other starting reagents were all analytically pure and used as received without further purification.

The praseodymium complexes with aromatic carboxylic acids were prepared by homogeneous precipitation. The pH value of the mixed ethanol/water solutions of aromatic carboxylic acids was adjusted to be about 6.5 using sodium hydroxide. After stirring, praseodymium nitrate were dipped into the solution and then white precipitates appeared. The resulting solid was filtered off, washed with ethanol and water, dried and stored over silica gel. The composition of the complexes was confirmed by elemental analyses and leads to  $\text{Pr}(\text{A})_3(\text{H}_2\text{O})_x$ , where A = benzoate (BA), 4-tert-butylbenzoate (TBBA), 2-benzoylbenzoate (BBA) and benzimidazole-5-carboxylate (BMC),  $x = 2\text{--}4$ . Anal. calcd for  $\text{C}_{21}\text{H}_{23}\text{O}_{10}\text{Pr}$ : C, 43.77; H, 4.02; Pr, 24.45; Found: C 44.21; H, 3.80; Pr, 24.16. Anal. calcd for  $\text{C}_{42}\text{H}_{31}\text{O}_{11}\text{Pr}$ : C, 59.17; H, 3.66; Pr, 16.53; Found: C, 58.86; H, 3.42; Pr, 16.45. Anal. calcd for  $\text{C}_{33}\text{H}_{43}\text{O}_8\text{Pr}$ : C, 55.94; H, 6.12; Pr, 19.88; Found: C 56.19; H, 5.84; Pr, 20.22. Anal. calcd for  $\text{C}_{24}\text{H}_{19}\text{N}_6\text{O}_8\text{Pr}$ : C, 43.65; H, 2.90; N, 12.73; Pr, 21.34; Found: C 43.23; H, 2.68; N, 12.96; Pr, 21.07.

### Physical measurement

Elemental analysis (C, H, N) was carried out by an Elementar Cario EL elemental analyzer. Infrared spectroscopy on KBr pellets was performed on a Nicolet Nexus 912 AO446 model spectrophotometer in the range of  $4000\text{--}400\text{ cm}^{-1}$ . Ultraviolet absorption spectra of these complexes ( $5 \times 10^{-4}\text{ mol L}^{-1}$  ethanol solution) were recorded with an Agilent 8453 spec-

trophotometer. Fluorescence (excitation and emission) spectra of these solid complexes and phosphorescence spectra ( $5 \times 10^{-4}\text{ mol L}^{-1}$  ethanol solution) at nitrogen atmosphere were determined with a Perkin–Elmer LS-55 spectrophotometer whose excitation and emission slits were 10 and 5 nm, respectively.

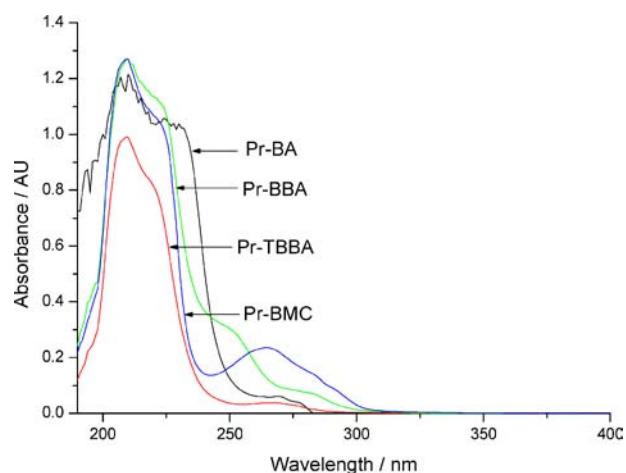
## Results and discussion

All the IR spectra of these praseodymium complexes show the similar features. For example, comparing the IR spectra of free HTBBA and its praseodymium complex, the characteristic absorption bands of  $\text{C}=\text{O}$  ( $1716.6\text{ cm}^{-1}$ ) and  $\text{C}-\text{O}$  ( $1334.0\text{ cm}^{-1}$ ) bands belonging to the free carboxylic acids disappear, while the characteristic absorption peaks of carboxylic group  $\text{COO}^-$  appear ( $1531.90$  and  $1413.39\text{ cm}^{-1}$ ), which suggest that the oxygen atoms of carbonyl groups of HTBBA (4-tert-butylbenzoic acid) are coordinated with  $\text{Pr}^{3+}$ . Besides, it can be observed that the absorption frequencies of  $\text{Pr}-\text{O}$  bond lie at around  $408\text{ cm}^{-1}$  in the low frequency of IR spectra for some praseodymium complexes. The apparent bands are noted at the range of  $3427.92$  and  $1601.36\text{ cm}^{-1}$  in IR spectra of praseodymium complexes, which are respectively attributed to the stretching vibration band and in-plane bending band of  $\text{H}_2\text{O}$  molecules. Furthermore, some in-plane swing vibration of coordinated  $\text{H}_2\text{O}$  molecules have been observed in the range of  $592.05\text{ cm}^{-1}$ , which verifies there exist both coordinated water molecules and crystal water molecules in these praseodymium complexes. Table 1 gives the detailed data for the main absorption bands and assignments.

Figure 1 shows the ultraviolet absorption spectra for praseodymium complexes with these four aromatic carboxylates, which shows the similar broad absorption band at the range of  $190\text{--}250\text{ nm}$  except for some band shifts of the maximum absorption ( $207\text{ nm}$  for Pr-BA,  $209\text{ nm}$  for Pr-TBBA,  $210\text{ nm}$  for Pr-BBA and  $210\text{ nm}$  for Pr-BMC, respectively), suggesting the characteristic absorption of phenyl cycle. Different benzoate derivatives with different substituted groups have influence on the electron distribution and the properties of electron donor and acceptor of the corresponding delocalized conjugated systems, which gives rise to the change of

**Table 1** The IR spectra data and their assignments for praseodymium complexes

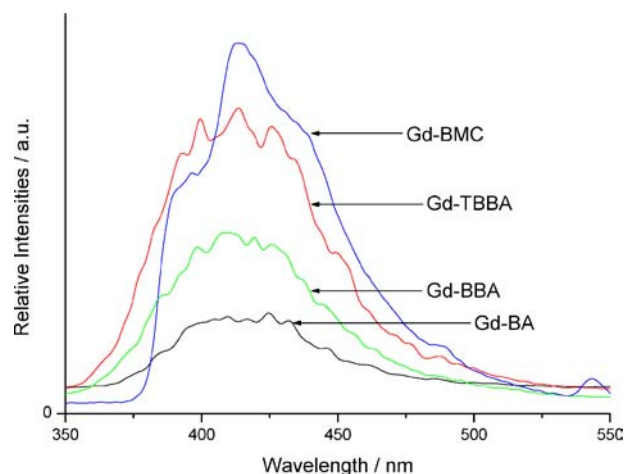
Complexes systems	$\nu_{\text{OH}}$ ( $\text{cm}^{-1}$ )	$\nu_{\text{S,COO}^-}$ ( $\text{cm}^{-1}$ )	$\nu_{\text{aS,COO}^-}$ ( $\text{cm}^{-1}$ )	$\nu_{\text{Pr-O}}$ ( $\text{cm}^{-1}$ )
$\text{Pr}(\text{BA})_3(\text{H}_2\text{O})_4$	3421.10	1532.24	1410.11	410.12
$\text{Pr}(\text{TBBA})_3(\text{H}_2\text{O})_2$	3427.92	1531.90	1413.39	420.43
$\text{Pr}(\text{BBA})_3(\text{H}_2\text{O})_2$	3391.54	1548.16	1397.63	420.11
$\text{Pr}(\text{BMC})_3(\text{H}_2\text{O})_2$	3207.96	1511.96	1405.98	424.39



**Fig. 1** Ultraviolet absorption spectra of praseodymium complexes of aromatic carboxylates

ultraviolet absorption and the band shift of ultraviolet spectra. With the introduction of substituted groups in phenyl cycle of benzoate, the electronic intensities decrease in the phenyl framework and the corresponding ultraviolet absorption band width of Pr-TBBA (BBA and BMC) shorten compared with that of Pr-BA. Besides this, there exist one weak absorption peak with maximum absorption wavelength at 265 nm in the ultraviolet spectrum of Pr-BMC, which can be ascribed the absorption of C–N in the midazole group in BMC.

Gd<sup>3+</sup> complex was selected as model complex for the determination of the triplet state energies of the organic ligands owing to their high phosphorescence – fluorescence ratio compared to those of the other Ln<sup>3+</sup> complexes and Gd<sup>3+</sup> can sensitize the phosphorescence emission of ligands. The low temperature phosphorescence spectra of these gadolinium complexes with aromatic carboxylic acids were measured at nitrogen atmosphere (77 K) (as shown in Fig. 2) and



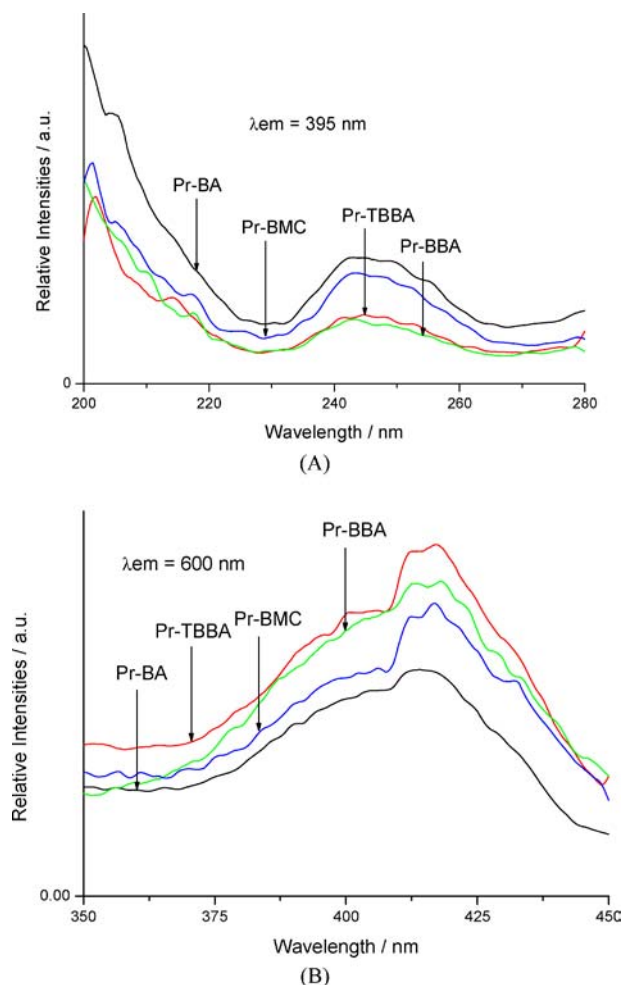
**Fig. 2** Phosphorescence spectra of gadolinium complexes of aromatic carboxylates at 77 K

**Table 2** The phosphorescence spectra data of gadolinium complexes

Complexes systems	Tr (Triplet-state energy) (cm <sup>-1</sup> )	ΔE (T <sub>1</sub> –Pr <sup>3+</sup> ) (cm <sup>-1</sup> )
Gd(BA) <sub>3</sub> (H <sub>2</sub> O) <sub>4</sub>	24750	7850
Gd(TBBA) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub>	24210	7310
Gd(BBA) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub>	23920	7020
Gd(BMC) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub>	24155	7255

the triplet-state energy of them can be determined based on the maximum phosphorescence band. The energy differences between the triplet state of aromatic carboxylic acids and the resonant energy level of Pr<sup>3+</sup> (<sup>4</sup>F<sub>9/2</sub>, about 16900 cm<sup>-1</sup>) can be calculated and the detailed data have been shown in Table 2. From these energy differences, it can be seen that all these ligands can sensitize praseodymium ion effectively. According to the intramolecular energy mechanism [39, 40], the intramolecular energy transfer efficiency depends chiefly on two energy transfer processes: the first one leads from the triplet level of ligands to the emissive energy level of the Ln<sup>3+</sup> ion by Dexter's resonant exchange interaction; the second one is just an inverse energy transfer by a thermal deactivation mechanism. Both energy transfer rate constants depend on the energy differences between the triplet level of the ligands and the resonant emissive energy of Ln<sup>3+</sup>. Intramolecular energy transfer efficiency in lanthanide complexes conforms to Dexter's exchange energy transfer theory [39]. On the other hand, there exist an inverse energy transfer process which affects fluorescence intensity by temperature [40]. From the low temperature phosphorescence spectra of these aromatic carboxylates, their triplet-state energies are 24000 cm<sup>-1</sup> or so and the resonant emissive energy level of Pr<sup>3+</sup> (<sup>1</sup>D<sub>2</sub>) is 16950 cm<sup>-1</sup> or so. So the energy differences from the triplet state energy of ligands and resonant emissive energy level of Pr<sup>3+</sup> is over 7000 cm<sup>-1</sup>, which is higher and energy match between them is not too suitable. It can be predicted that the fluorescence intensities corresponded to the intramolecular energy transfer process of corresponding praseodymium complexes will be not too strong in spite of the existence of "antenna effect." Certainly the energy transfer is only one factor determining the fluorescence properties of lanthanide complexes, which also depend on the structure of ligands.

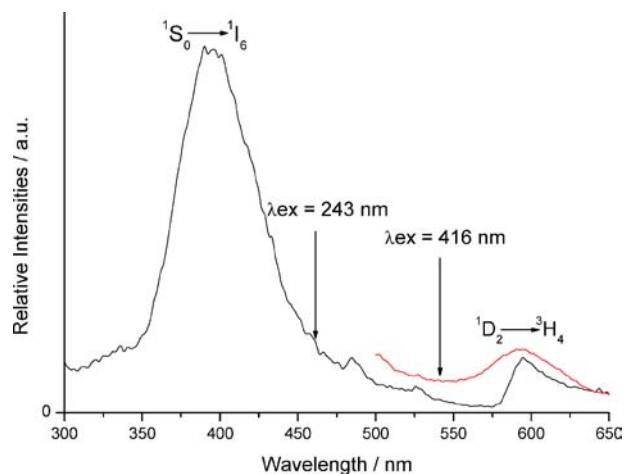
The excitation spectra of these complexes show that there is two effective absorption bands in the 200–450 nm UV–vis region. Figure 3 gives the representative excitation spectra of some praseodymium complexes. The first effective energy absorption mainly takes place in the narrow ultraviolet region of 200–280 nm with maximum excitation peaks at around 245 nm, which may belong to the charge transfer state of Pr<sup>3+</sup> transition and the π → π\* transition of ligands (Pr–O). The second apparent excitation band occurs in long wavelength ultraviolet-violet region, at the range of



**Fig. 3** Selected excitation spectra of some praseodymium complexes (A) short wavelength ultraviolet region. (B) long wavelength region

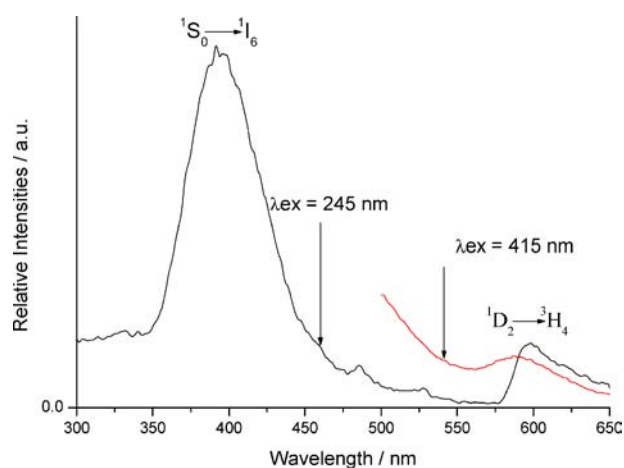
nm with the maximum wavelength of about 415 nm, this is attributed as the  $4f \rightarrow 4f$  transition of  $\text{Pr}^{3+}$  corresponded to  ${}^3\text{H}_4 \rightarrow {}^3\text{P}_2$ . We further measured the corresponding emission spectra by selective excitation into the four different components; they show a similar emission position except for different fluorescent intensities.

Voloshin *et al.* [38] reported the luminescence of praseodymium (III) chelates from two excited states ( ${}^3\text{P}_0$  and  ${}^1\text{D}_2$ ) and its dependence on ligand triplet state energy. They found that praseodymium (III) *b*-diketonate and carboxylate chelates emit visible and infrared luminescence in organic solutions at room temperature, depending on the position of triplet level of the ligand [38]. We measured the selected emission spectra of solid-state praseodymium complexes of 2-benzoylbenzoate (Fig. 4) and benzimidazole-5-carboxylate (Fig. 5), respectively. These fluorescence spectra show two apparent emission peaks under excitation at 245 nm: one stronger emission is located at ultraviolet to violet region of 395 nm and the other weaker emission at orange region around 595 nm, corresponding to the charac-



**Fig. 4** Emission spectra of praseodymium complex of 2-benzoylbenzoate

teristic  ${}^1\text{S}_0 \rightarrow {}^1\text{I}_6$  and  ${}^1\text{D}_2 \rightarrow {}^3\text{H}_4$  transition of  $\text{Pr}^{3+}$  ion. The detailed data about the relative intensities for the violet and orange emission of  $\text{Pr}^{3+}$  in their complexes were summarized in Table 3. Under the excitation of long wavelength of 415 nm, these Pr complexes only wear the single-emission band of 595 nm ascribed to the  ${}^1\text{D}_2 \rightarrow {}^3\text{H}_4$  transition of  $\text{Pr}^{3+}$ .  ${}^1\text{S}_0 \rightarrow {}^1\text{I}_6$  transition belongs to the emission from the charge transfer state, which is due to the result that electronic density distributes from the molecular orbital to the ion orbital of  $\text{Pr}^{3+}$ . Therefore, the corresponding ultraviolet–violet fluorescence possesses the stronger intensity. While  ${}^1\text{D}_2 \rightarrow {}^3\text{H}_4$  transition is the characteristic spectrum originated from the  $f \rightarrow f$  transition of  $\text{Pr}^{3+}$ , resulting in the weaker yellow–orange emission. As we know, the ground state spectral term of  $\text{Pr}^{3+}$  is  ${}^3\text{H}_4$  and other excited state spectral terms are  ${}^3\text{H}_5$ ,  ${}^3\text{H}_6$ ,  ${}^3\text{F}_2$ ,  ${}^3\text{F}_3$ ,  ${}^3\text{F}_4$ ,  ${}^1\text{G}_4$ ,  ${}^1\text{D}_2$ ,  ${}^3\text{P}_0$ ,  ${}^3\text{P}_1$ , and  ${}^3\text{P}_2$ , respectively. Different transition from the different excited state to ground state can give rise to different spectra. In our



**Fig. 5** Emission spectra of praseodymium complex of with benzimidazole-5-carboxylate

**Table 3** The fluorescence intensities of praseodymium complexes of aromatic carboxylic acids

Complexes systems	$\lambda_{\text{ex}}$ (nm)	$^1\text{S}_0 \rightarrow ^1\text{I}_6$ ( $\text{cm}^{-1}$ )	$^1\text{D}_2 \rightarrow ^3\text{H}_4$ ( $\text{cm}^{-1}$ )	$\lambda_{\text{ex}}$ (nm)	$^1\text{D}_2 \rightarrow ^3\text{H}_4$ ( $\text{cm}^{-1}$ )
Pr(BA) <sub>3</sub> (H <sub>2</sub> O) <sub>4</sub>	245	25315	601	415	601
Pr(TBBA) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub>	245	25445	593	415	598
Pr(BBA) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub>	243	25250	595	415	595
Pr(BMC) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub>	243	25315	595	415	595

measurements, we also found the one weaker emission of  $^1\text{D}_2 \rightarrow ^3\text{H}_4$  transition of  $\text{Pr}^{3+}$  for these complexes, suggesting the intramolecular energy transfer process still exist between the triplet state energy of aromatic carboxylates to the resonant emissive energy level of  $\text{Pr}^{3+}$ , i.e. “antenna effect.” The energy of  $^3\text{P}_2$  and  $^3\text{P}_1$  are so high that the intramolecular energy transfer process cannot take place. All these praseodymium complexes exhibit the weaker fluorescence intensities of  $^1\text{D}_2 \rightarrow ^3\text{H}_4$  transition, which take agreement with the prediction from the energy match and energy transfer.

## Conclusions

In summary, the fluorescent properties of four praseodymium complexes of benzoate derivatives have been studied. The energy match and intramolecular energy transfer between aromatic carboxylic acids and praseodymium ions were discussed in detail, which indicate that there exist the large energy differences between the triplet state energies of aromatic carboxylates and the resonant emission energy level of  $\text{Pr}^{3+}$  and the corresponding luminescent intensities of them corresponding complexes are weak. Subsequently, the emission at the ultraviolet–violet region shows the higher luminescence for the charge transfer state of Pr–O (LMCT). These praseodymium complexes can realize the double light frequency conversion in both ultraviolet (from 245 to 415 nm) and visible region (from 415 to 595 nm), which can be expected to have potential application in fluorescent probe or sensors.

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