PAPER

NIR luminescence of a series of benzoyltrifluoroacetone erbium complexes†

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A series of five β-diketone erbium complexes with various azacyclo-auxiliary ligands, namely, $Er(Hbta)_3(H_2O)_2$ (**1**), $Er(Hbta)_3(bpy)$ (**2**), $Er(Hbta)_3(phen)$ (**3**), $Er(Hbta)_3(dpq)$ (**4**) and $Er(Hbta)_3(dppz)$ (**5**) (Hbta = benzoyltrifluoroacetone, bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline, dpq = pyrazino [2,3-*f*][1,10]phenanthroline, dppz = dipyrido[3,2-*a*:2′,3′-*c*]phenazine) have been isolated and characterized by X-ray crystallographic analysis. Near-infrared luminescence analysis reveals that all complexes **1–5** exhibit strong NIR luminescence of Er(III) ions around 1535 nm with the highest lifetime of 4.532 μs, quantum yield of 3.24×10^{-4} and broadband emission around 1.5 μm for complex **5**, in which the azacyclo-auxiliary ligand absorbs and transfers the energy leading to complete quenching of the ligand-associated visible emission. The energy transfer processes among benzoyltrifluoroacetone, the Er(III) ion and the auxiliary ligands in complexes **1–5** have been investigated.

Introduction

Lanthanide ion emissions in the near-infrared region (NIR) of the spectrum, such as Er(III), Nd(III), Yb(III), Pr(III) and Sm(III) ions, have received increasing attention for their potential applications in telecommunications, optical communication systems, optical amplifiers and fluoroimmunoassays.[1] Particularly, the Er(III) ion has attracted considerable attention on the basis of its emission in the C-band (1.53–1.565 mm) of the silica optical telecommunication window[2] since Weissman reported that lanthanide β-diketonate complexes exhibit luminescence when irradiated with ultraviolet light in 1942.[3] After that, more and more studies on NIR luminescence of β-diketonate Er(III) complexes have been documented.[4] For instance, the complexes $Er(tpm)_3(bipy)$,[4i] $Er(tpm)_3(bath)$,[4i] $Er(tpm)_3(5NO_2phen)$,[4i] $Er(tfac)_3(bipy)$,[4j] $Er(tfac)_3(bath)$[4j] and $Er(tfac)_3(5NO_2phen)$,[4j] (1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione = tpm, 1,1,1-trifluoro-2,4-pentanedione = tfac, 2,2′-bipyridine = bipy, bathophenanthroline = bath, 5-nitro-1,10-phenanthroline = 5NO₂-phen) have been isolated and they all show the characteristic near-infrared (NIR) luminescence of the corresponding Er(III) ions. It is known that the replacement of C–H bonds with lower-energy C–F oscillators is able to lower the vibration energy of the ligand, which in turn decreases the energy loss caused by ligand vibrations and enhances the emission intensity of the Er(III) ion.[5] And the rigid ligand restricts the thermal vibration of the complexes and reduces the loss of energy by nonradiative decay.[6] Meanwhile, different rigid azacyclo-auxiliary ligands were added to increase the conjugated π-electron fragments and replace the solvent molecules to promote the excited state lifetime and quantum yield.[7] Furthermore, the azacyclo-auxiliary also determines the efficiency of the antenna effect, leading to quenching of the ligand-associated visible emission and enhancing the NIR emission.[4i,4j] Therefore, choosing appropriate ligands to increase the lifetime and quantum yield of Er(III) complexes is still a challenge. Herein, attempting to develop the NIR luminescence of β-diketone erbium complexes, the β-diketone of benzoyltrifluoroacetone (Hbta) containing rigid phenyl and CF₃ groups was employed in the reactions with $ErCl_3 \cdot 6H_2O$ and azacyclo ligand. As a result, a series five Hbta Er(III) complexes **1–5** with different auxiliary ligands have been isolated (Scheme 1). Their crystal structures and near-infrared luminescence have been investigated.

Experimental

Materials and instrumentation

All chemicals except $ErCl_3 \cdot 6H_2O$ were obtained from commercial sources and used without further purification. $ErCl_3 \cdot 6H_2O$ was prepared by the reaction of Er_2O_3 and hydrochloric acid in aqueous solution. The benzoyltrifluoroacetone was obtained by J&K Chemical. FT-IR spectra were run on a Perkin-Elmer 100 spectrophotometer in the range of 4000–450 cm⁻¹. UV spectra (in CH_3OH) were performed on a Perkin-Elmer Lambda 35

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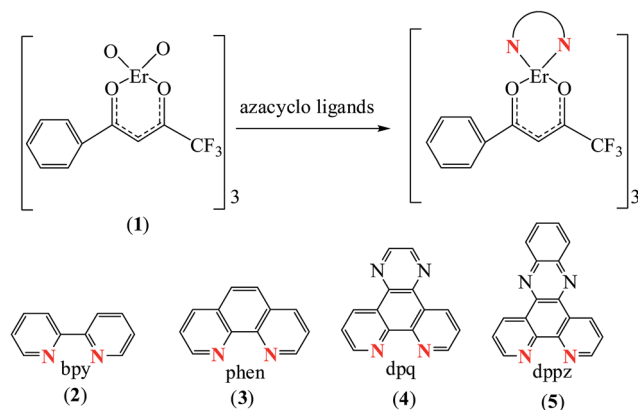
Scheme 1 Synthesis of complexes **1–5**.

spectrometer. Thermal analyses were conducted on a STA-6000 instrument in the temperature range 30–800 °C with a heating rate of 10 °C min^{-1} under atmosphere. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku D/Max-3B X-ray diffractometer with Cu Kα radiation, the scanning rate is 4°/s, 2θ ranging from 5–50°. Excitation and emission spectra were measured with an Edinburgh FLS 920 fluorescence spectrophotometer. Luminescence lifetimes were recorded on a single photon counting spectrometer from Edinburgh Instrument (FLS 920) with microsecond pulse lamp as the excitation.

Synthesis of complexes 1–5

Er(Hbta)$_3$(H$_2$O)$_2$ (1). NaOH (0.08 g, 2 mmol) and Hbta (0.43g, 2 mmol) in methanol was stirred for 15 min. Then, ErCl$_3$·6H$_2$O (0.25 g, 0.65 mmol) was added to the solution and the mixture was stirred for 24 h at room temperature. Water was then added to the solution; a suspension was formed immediately which was then filtered to remove the suspended particles. These particles were washed with water and dried in air. Single crystals were harvested in about 3 weeks from dichloromethane/hexane. Yield: 692.7 mg (82%). Elemental analysis: (%) calcd for C$_{30}$H$_{22}$ErF$_9$O$_8$ (848.74): C, 42.45; H, 2.61. Found: C, 42.46; H, 2.60. IR (KBr, ν/cm^{-1}): 3186 (w), 1620 (s), 1528 (s), 1320 (s), 1273 (s), 1138 (s), 1006 (m), 853 (m), 777 (s). UV-vis (CH$_3$OH, λ_{max}/nm): 326, 257.

Complex **2–5** were prepared by stirring equimolar solutions of complex **1** and the nitrogen donor in CH$_3$OH for 24 h at ambient temperature (Scheme 1). The raw products were isolated according to the aforementioned method. Single crystals were obtained in about several days by recrystallization from dichloromethane/hexane.

Er(Hbta)$_3$(bpy) (2). Yield: 794 mg (82%). Elemental analysis: (%) calcd for C$_{40}$H$_{26}$ErF$_9$N$_2$O$_6$ (968.89): C, 49.59; H, 2.70; N, 2.89. Found: C, 49.60; H, 2.70; N, 2.88. IR (KBr, ν/cm^{-1}): 2935 (w), 1627 (s), 1530 (s), 1360 (m), 1293 (s), 1195 (m), 1132 (s), 1014 (m), 853 (m), 769 (s). UV-vis (CH$_3$OH, λ_{max}/nm): 322, 260.

Er(Hbta)$_3$(phen) (3). Yield: 864 mg (87%). Elemental analysis: (%) calcd for C$_{42}$H$_{26}$ErF$_9$N$_2$O$_6$ (992.91): C, 50.81; H, 2.64; N, 2.82. Found: C, 50.80; H, 2.65; N, 2.81. IR (KBr, ν/cm^{-1}): 2925

(w), 1627 (s), 1522 (s), 1363 (m), 1294 (s), 1223 (m), 1132 (s), 1014 (m), 847 (m), 777 (s). UV-vis (CH$_3$OH, λ_{max}/nm): 323, 262.

Er(Hbta)$_3$(dpq) (4). Yield: 835.9 mg (80%). Elemental analysis: (%) calcd for C$_{44}$H$_{26}$ErF$_9$N$_4$O$_6$ (1044.95): C, 50.57; H, 2.51; N, 5.36. Found: C, 50.56; H, 2.52; N, 5.35. IR (KBr, ν/cm^{-1}): 2935 (w), 1627 (s), 1530 (s), 1360 (m), 1293 (s), 1195 (m), 1132 (s), 1014 (m), 853 (m), 769 (s). UV-vis (CH$_3$OH, λ_{max}/nm): 322, 252.

Er(Hbta)$_3$(dppz) (5). Yield: 952.6 mg (87%). Elemental analysis: (%) calcd for C$_{48}$H$_{28}$ErF$_9$N$_4$O$_6$ (1095.0): C, 52.65; H, 2.58; N, 5.12. Found: C, 52.66; H, 2.57; N, 5.13. IR (KBr, ν/cm^{-1}): 2925 (w), 1627 (s), 1522 (s), 1363 (m), 1294 (s), 1223 (m), 1132 (s), 1014 (m), 847 (m), 777 (s). UV-vis (CH$_3$OH, λ_{max}/nm): 321, 268.

Determination of the crystal structures

X-ray single-crystal diffractions of complexes **1–5** were performed at 293 K on an Oxford Xcalibur Gemini Ultra diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Empirical absorption corrections on the basis of equivalent reflections were applied. The structures of **1–5** were solved by direct methods and refined with a full-matrix least squares technique. All non-hydrogen atoms were refined. All crystal data and refinement parameters for complexes **1–5** are summarized in Table 1.

Results and discussion

Descriptions of complexes 1–5

Crystal structure analysis shows that all complexes **1–5** are mononuclear. The Er(III) ion in complex **1** is eight-coordinated with six oxygen atoms from three bidentate Hbta ligands, the other two coordination sites from two H$_2$O molecules in a distorted dodecahedron geometry (Fig. 1a and b) in which the average Er–O distance is 2.334 Å. While the Er(III) ion in complexes **2–5**, is eight-coordinated by six O atoms from the Hbta ligands and two N atoms from the different azacyclo-ligand (Fig. 1c, e, g and i) in a distorted square-antiprismatic geometry (Fig. 1d, f, h and j). The average Er–N distances in complexes **2–5** are 2.514, 2.540, 2.528 and 2.507 Å, respectively.

TG-DSC analysis of complexes 1–5

TG-DSC analysis for complex **1** exhibits a gradual weight loss of 4.2% in the first step, 95–160 °C, which corresponds to the loss of two coordinate water molecules (Fig. S1, ESI†). In contrast, there is no weight loss observed for complexes **2–5** before 300 °C hinting that there are no solvents in complexes **2–5** (Fig. S1–3, ESI†).

Spectral analysis of complexes 1–5

The IR spectrum of complex **1** exhibits the typical broad absorption in the region 3000–3500 cm^{-1}, proposing the presence of water molecules (Fig. S7, ESI†). In contrast, the absence of the broad bands in the region 3000–3500 cm^{-1} for complexes **2–5** suggests that water molecules in complex **1** have been displaced by the nitrogen donor. The UV-vis absorption spectra of the free ligand Hbta and complexes **1–5** were conducted in CH$_3$OH solution ($c = 1 \times 10^{-5}$ M). The absorption spectrum of

Table 1 Crystal data and structure refinement details for complexes 1–5

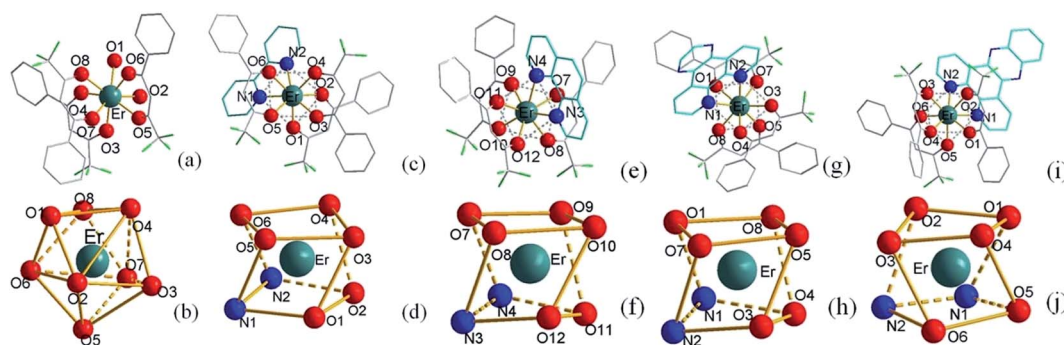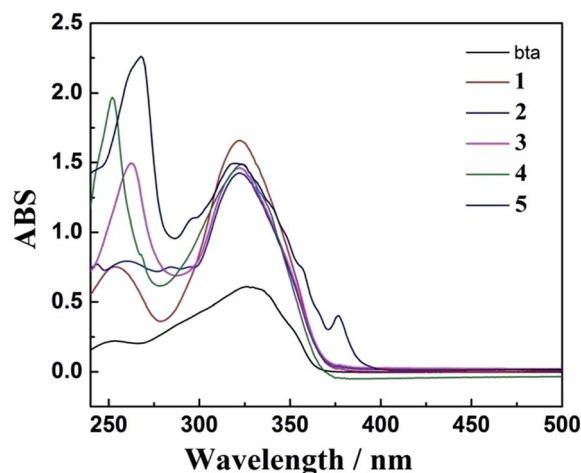| Complexes	1	2	3	4	5
Empirical formula	$C_{30}H_{22}ErF_9O_8$	$C_{40}H_{26}ErF_9N_2O_6$	$C_{42}H_{26}ErF_9N_2O_6$	$C_{44}H_{26}ErF_9N_4O_6$	$C_{48}H_{28}ErF_9N_4O_6$
Formula weight	848.74	968.89	992.91	1044.95	1095.0
Color	Pink	Pink	Pink	Pink	Pink
Crystal system	Orthorhombic	Monoclinic	Triclinic	Orthorhombic	Tetragonal
Space group	$P2_12_12_1$	$P2_1/c$	$P\bar{1}$	$Pna2_1$	$P4/n$
a (Å)	10.697(5)	11.116(5)	10.009(5)	21.392(5)	28.129(5)
b (Å)	13.011(5)	22.589(5)	13.987(5)	10.941(5)	28.129(5)
c (Å)	22.764(5)	17.170(5)	14.769(5)	18.213(5)	11.620(5)
α (deg)	90.000(5)	90.00	82.932(5)	90.000(5)	90.000(5)
β (deg)	90.000(5)	114.870(19)	87.086(5)	90.000(5)	90.000(5)
γ (deg)	90.000(5)	90.00	76.531(5)	90.000(5)	90.000(5)
V (Å^3)	3168(2)	3912(2)	1994.9(14)	4263(2)	9194(5)
Z	4	4	2	4	8
ρ (g cm^3)	1.780	1.645	1.653	1.628	1.582
μ (mm^{-1})	2.750	2.237	2.195	2.060	1.915
F (000)	1660	1908	978	2060	4328
R_1 ($I > 2\sigma(I)$)	0.0270	0.0393	0.0411	0.0411	0.0517
wR_2 ($I > 2\sigma(I)$)	0.0558	0.0872	0.0946	0.0982	0.1149
R_1 (all data)	0.0244	0.0543	0.0496	0.0499	0.0998
wR_2 (all data)	0.0545	0.0970	0.1016	0.1051	0.1328
GOF on F^2	1.055	1.069	1.037	1.051	1.003

Fig. 1 Molecular structures of complexes 1–5 and the local coordination geometries of Er(III) ions for complexes 1–5 (hydrogen atoms are omitted for clarity).

Hbta, shows two maxima at 326 nm and 254 nm (Fig. 2), which can be attributed to singlet–singlet ($^1\pi$–π*) enol absorption[8] of Hbta and the singlet–singlet ($^1\pi$–π*) transitions in the phenyl rings,[9] respectively. The absorption spectra of complexes 1–5 are similar to that of Hbta except for a blue-shifted of the shoulder at 326 nm to 322 nm and a red-shifted of the shoulder at 254 nm to 260 nm, which result from the perturbation induced by the coordination of Er(III) ion.

Photoluminescence in the solid state of complexes 1–5

The emission from Hbta of complexes 1–5 in the visible region, have been observed in Fig. 3 left. The emission intensities are in the sequence of 1 > 2 > 3 > 4 > 5. It is attributed to that the quenching of the visible emission of complexes 1–5 are related to the efficiency of the energy transfer capability from the azacyclo-auxiliary ligand to Er(III) ion. While, the emission from Er(III) ion of complexes 1–5 in the NIR region exhibit the maximum peaks around 1535 nm covering a large spectral

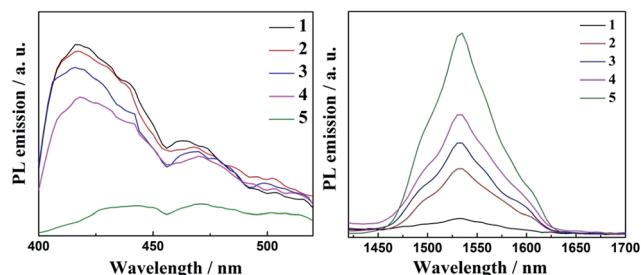Fig. 2 UV absorption spectra of Hbta and complexes 1–5 in CH$_3$OH solution ($c = 1 \times 10^{-5}$ M).

Fig. 3 PL emissions in the visible region (left) and the near-infrared region (right) of complexes 1–5 in powder.

Table 2 Photophysical parameters of complexes **1–5** and their Er(III) analog

Complexes	Fwhm/nm	$\tau/\mu s$	$\varphi/10^{-4}$	Refs
Er(Hbta)$_3$(H$_2$O)$_2$ (**1**)	75	1.173	0.83	
Er(Hbta)$_3$(bpy) (**2**)	76	1.192	0.85	
Er(Hbta)$_3$(phen) (**3**)	78	2.062	1.47	
Er(Hbta)$_3$(dpq) (**4**)	82	3.268	2.33	
Er(Hbta)$_3$(dppz) (**5**)	79	4.532	3.24	
Er(tpm)$_3$(5-NO$_2$phen)	—	1.53	—	4i
Er(tpm)$_3$(bipy)	—	1.77	—	4i
Er(tpm)$_3$(bath)	—	1.55	—	4i
Er(tfac)$_3$(bpy)	—	1.65	—	4j
Er(tfac)$_3$(bath)	—	1.40	—	4j
Er(tfac)$_3$(5-NO$_2$phen)	—	1.35	—	4j
Er(dmh)$_3$(bpy)	65	1.67	—	4k
Er(dmh)$_3$(bath)	60	1.69	—	4k
Er(dmh)$_3$(5-NO$_2$phen)	58	1.38	—	4k
Er(dnm)$_3$(5NO$_2$phen)	—	1.57	—	4n
Er(acac-F$_7$)$_3$(OP(C$_6$F$_5$)$_3$)$_2$	—	16.8	17	4l

range from 1450 to 1630 nm (Fig. 3 right), which are attributed to the typical $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er(III) ion.[10] The excitation spectra of complexes **1–5** were shown in Fig. S8.† Notably, the NIR emission intensities are in the sequence of **5 > 4 > 3 > 2 > 1**. The NIR luminescent decay curves of complexes **1–5** (Fig. 4) are well fitted by a monoexponential function, which indicates the presence of a single luminescent site.[11] The lifetime are in the queue of **5 > 4 > 3 > 2 > 1**. The intrinsic quantum yields of complexes **1–5** were calculated by using the eqn (1).

$$\phi_{Ln} = \tau_{obs}/\tau_{rad} \tag{1}$$

where τ_{obs} is the observed lifetime and τ_{rad} is "natural" lifetime of the Ln(III). The reported radiative (natural) lifetime for Er(III) is 14 000 μs.[4a] The relative quantum yield of complexes **1–5** are calculated and listed in Table 2. Obviously, the relative quantum yields are the same as the intensity in the sequence of **5 > 4 > 3 > 2 > 1**.

Notably, the NIR luminescent intensities, lifetime and relative quantum yields for complexes **1–5** exhibit the coincident tendency of **5 > 4 > 3 > 2 > 1**. Which are correlated to the conjugate system of the azacyclo-auxiliary ligands and the distances of Er–N bonds,[4i,4j] namely, the larger conjugate system and the shorter Er–N bonds, the stronger the NIR intensity.
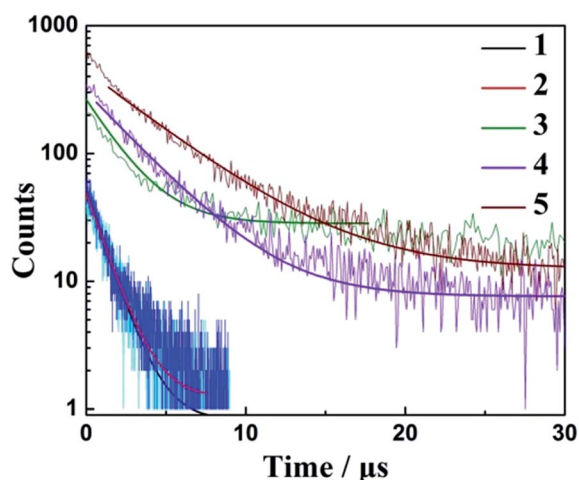

Fig. 4 Luminescence decay profiles for complexes 1–5 in solid state at 298 K.

While, all the emission intensities for complexes **2–5** are higher than that for complex **1** inasmuch as the auxiliary ligands replace the coordination solvent molecules for minimizing the non-radiative deactivation. In comparison with previously reported Er(III) analog, the lifetime and relative quantum yield of complex **5** is apparently higher than those for Er(tpm)$_3$(bipy), Er(tpm)$_3$(bath), Er(tpm)$_3$(5NO$_2$phen),[4i] Er(tfac)$_3$(bipy), Er(tfac)$_3$ (bath) and Er(tfac)$_3$(5NO$_2$phen),[4j] suggesting that the large conjugate auxiliary ligand dppz is able to enhance the NIR luminescence by way of tuning the intramolecular energy transfer efficiency. However, the lifetime and relative quantum yield of complex **5** are lower than 16.8 μs and 1.7×10^{-3} for complex [Er(acac-F$_7$)$_3$(OP(C$_6$F$_5$)$_3$)$_2$][4l] suggesting that the completely fluorinated β-diketone ligand Hacac-F$_7$ (1,1,1,3,5,5,5-heptafluoropentane-2,4-dione) dominates the NIR luminescence by decreases the energy loss caused by ligand vibrations.

Intramolecular energy transfer between ligands and Er(III) ions

To elucidate the energy transfer processes in the complexes **1–5**, the energy levels of the relevant electronic states are estimated. The singlet and triplet energy levels of Hbta and bidentate nitrogen donors are estimated by referring to their wavelengths of UV-vis absorbance edges and the lower wavelength emission peaks of the corresponding phosphorescence spectra. The triplet energy level of Gd(Hbta)$_3$(H$_2$O)$_2$, which corresponds to the lower emission peak wavelength, is 21 600 cm^{-1} (464 nm). The single state energy ($^1\pi\pi^*$) level of Hbta is estimated by referencing its absorbance edge, which is 26 700 cm^{-1} (375 nm). The singlet and triplet energy levels of bpy (29 900 and 22 900 cm^{-1}), phen (31 000 and 22 100 cm^{-1}), dpq (34 500 and 21 200 cm^{-1}) and dppz (37 000 and 18 600 cm^{-1}) were taken from the literature.[12] To further understand the energy transfer process between the primary ligand Hbta and the auxiliary ligands, the schematic energy level diagram and the energy transfer process for complex **2**, as an typical example, is shown in Fig. 5. The triplet levels ($^3\pi\pi^*$) of the ligand Hbta
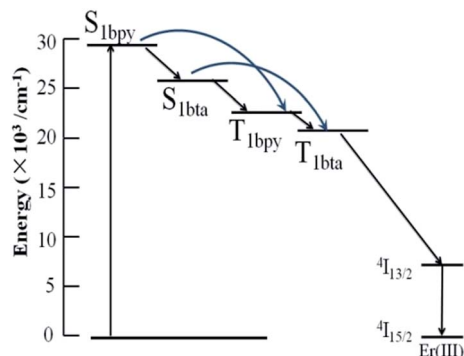
Fig. 5 Schematic energy level diagram and energy transfer process for complex **2**. S_1, first excited singlet state; T_1, first excited triplet state.

(21 600 cm^{-1}), bpy (22 900 cm^{-1}), phen (22 100 cm^{-1}), dpq (21 200 cm^{-1}) and dppz (18 600 cm^{-1}) are obviously higher than the $^4I_{13/2}$ level (6500 cm^{-1}) of Er(III) ion, and their energy gaps $\Delta E\,(^3\pi\pi^*-^4I_{13/2})$ are 15 100, 16 400, 15 600, 14 700, 12 100 cm^{-1}, respectively, which are too high to allow an effective back energy transfer. The energy gap between the $^1\pi\pi^*$ and $^3\pi\pi^*$ states of Hbta, bpy, phen, dpq and dppz are 5100, 7000, 8900, 13 300, 18 400 cm^{-1}, respectively. According to Reinhoudt's empirical rule,[13] the intersystem crossing process becomes effective when $\Delta E\,(^1\pi\pi^*-^3\pi\pi^*)$ is at least 5000 cm^{-1}. Therefore, the effective intersystem crossing and ligand to metal energy transfer processes can be found in all complexes **1–5**, which demonstrated that the ligands are suitable for sensitizing the Er(III) ion luminescence. Strikingly, the NIR luminescence of Er(III) complexes are particularly interesting for application in optical amplifiers since the transition around 1535 nm is in the right position for the third telecommunication window.[2] To enable a wide gain bandwidth for optical amplification, a broad emission band is desirable.[14] The full width at half maxima (FWHM) of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transitions for the complexes **1–5** are in the range of 75–82 nm (Table 2), which are of potential application in optical amplification.

Conclusion

Isolation of a series of five β-diketone Er(III) complexes **1–5** verifies that β-diketone benzoyltrifluoroacetone (Hbta) is able to afford mononuclear eight-coordinated Er(III) complexes with various azacyclo-auxiliary ligands. Systematic investigations on their NIR luminescence of complexes **1–5** unambiguously demonstrate that the Hbta ligand is an effective sensitizer on NIR luminescence of Er(III) ions, and the azacyclo-auxiliary ligands can further enhance the lifetimes and quantum yields through the energy transfer among the molecular orbits of the ligand, azacyclo-auxiliary ligands and Er(III) ion in which the larger conjugate system of the ligand and the shorter Er–N bonds, the stronger the NIR intensity. Strikingly, complex **5** exhibit unique NIR luminescent quantum yield among the reported β-diketone Er(III) complexes, The broadband emission around 1.5 μm for complexes **1–5** may provide potential material in optical amplifiers.

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