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PAPER

A New Heterometallic Terbium(III)-Ruthenium(II) Complex and its Terbium(III)-Zinc(II) Analog: Syntheses, Characterization, Luminescence, and Electrochemical properties†

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Synthesis of a *d-f* heterometallic trinuclear complex $[Tb(NO_3)_2(L^2)\{Ru(ttpy)\}_2](PF_6)_5$ (**6**) (**L^2** = N^1,N^2-bis(2-((Z)-2-(4-(2,2′:6′,2″)-terpyridin-4′-yl-benzyloxy)benzylideneamino)ethyl)ethane-1,2-diamine; ttpy = 4′-tolyl-2,2′:6′,2″-terpyridine) and intramolecular energy transfer from terbium(III) to ruthenium(II) at room temperature are reported. 2-(4-(2,2′:6′,2″)-Terpyridin-4′-yl-benzyloxy)benzaldehyde (**L^1**) is characterized by X-ray diffraction: triclinic, $P\bar{1}$. The terbium(III) complex $[Tb(NO_3)_2(L^2)]NO_3.5H_2O$ (**2**) is synthesized by the Schiff base condensation of triethylenetetraamine with **L^1** in the presence of $Tb(NO_3)_3.5H_2O$ as template as well as by the reaction of the preformed Schiff base **L^2** with $Tb(NO_3)_3.5H_2O$. The dinuclear complex $[\{Ru(ttpy)\}_2(L^2)](PF_6)_4$ (**5**) is synthesized by the Schiff base condensation of triethylenetetraamine with the mononuclear complex $[Ru(L^1)(ttpy)](PF_6)_2$ (**4**). The terbium(III) complex **2** exhibits a set of seven emission bands at 490, 545, 585, 622, 651, 668, and 684 nm characteristic of the $^5D_4 \rightarrow {}^7F_{0-6}$ transitions of terbium(III). The Tb^{III}-Ru^{II} *d-f* heterometallic complex **6** exhibits emission at 687 nm characteristic of the ruthenium(II) tolylterpyridine molecular components. Ruthenium(II) luminescence is sensitized at room temperature by the intramolecular intercomponent energy transfer from the luminescent $^5D_4$ metal centered excited state of terbium(III) to the ^{3}MLCT state of ruthenium(II) with a concomitant increase in the ruthenium(II) luminescence lifetime of 1.20 ns. The Tb^{III}-Zn^{II} heterometallic assembly $[Tb(NO_3)_2(L^2)\{Zn(ttpy)\}_2](PF_6)_5$ (**7**) exhibits emission bands characteristic of the terbium(III) center. The results indicate photoinduced intramolecular energy transfer from the ttpy moieties of the $[Zn(ttpy)_2]^{2+}$ molecular components to the terbium(III) center. The study demonstrates the use of terpyridine derivative appended terbium(III) complex as a synthon for the construction of heterometallic *d-f* assemblies. The two ruthenium(II) centers of **6** undergo electrochemical oxidation at the same potential ($E_{1/2}$ for the Ru(II)/Ru(III) redox couple is 0.93 V) indicating their electrochemical equivalence.

Introduction

Lanthanides are an interesting class of luminescent metal ions[1] which find continuing use[2] for the engineering of lamp phosphors,[3] optical fiber lasers and amplifiers for telecommunications,[4] for the creation of electroluminescent materials[4] and functional molecular and supramolecular assemblies,[5] and in molecular recognition.[6] Luminescent lanthanide complexes constitute an important class of optical probes for sensing bio-active species,[7] high throughput assays and screening protocols in vitro[8] and in time-resolved imaging studies in cellulo.[7,9]

The shielding of the 4*f*-orbitals by the filled $5p^6$, $6s^2$ orbitals results in special spectroscopic properties with parity forbidden 4*f*-4*f* transitions. As a result, the absorption coefficients are very low (typically 1-10 L mol^{-1} cm^{-1}), the lifetimes of the excited states are relatively long,[10] and the emissive rates are slow which result in long-lived and narrow line-like emission bands.[11] As a consequence, direct excitation of the Ln(III) ions rarely yields highly luminescent materials. Lanthanide ions are, therefore, complexed with ligands bearing sensitizing chromophores capable of transferring their excited state energy to the encapsulated metal ions. These chromophores need to be engineered onto the ligands and serve as antenna to harvest incident

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light. Detailed study of their structural and mechanistic features have been reviewed.[8c,9a,b,g-j,12] Most of the investigations have been devoted to europium(III) and terbium(III) compounds due to their large Stokes shifts and long luminescence lifetimes in the order of milliseconds[13] and strong emission in the visible spectral region and are used as sensors,[9g,14] as luminescent labels in fluoroimmunoassay and time-resolved microscopy[15] and for the construction of photochemical supramolecular devices and machines.[16]

The luminescence and redox properties of ruthenium(II), osmium(II), and rhenium(I) complexes of 2,2′-bipyridine (bpy) and related bidentate ligands have been extensively studied[17] and employed as building blocks for the construction of photochemical supramolecular assemblies. Ruthenium(II) bipyridine based acyclic, macrocyclic and calix[4]arene ligand frameworks have been used for sensing or labeling purposes.[18] Complexes of bidentate bpy-type ligands including $[M(bpy)_3]^{n+}$ are chiral and exist in two enantiomeric forms. Asymmetrically functionalized bipyridines may lead to the formation of isomers for each tris(homoleptic) complex with no control over the geometry of the systems.[19] In contrast, $[M(tpy)_2]^{n+}$ (tpy = 2,2′:6′,2″-terpyridine) is achiral, but does not luminesce at room temperature. Introduction of substituents at the 4′-position of tpy improves the luminescence of their complexes.[20] Complexes of functionalized terpyridine-based ligands have been increasingly used as scaffolds in the assembly of metallosupramolecules,[21] functional nanomaterials and devices,[21a] and light-emitting electrochemical cells,[22] and as sensitizers for solar cells.[23]

Near IR emitting *d-f* hybrid molecular edifices[24] have been attracting considerable attention because of their potential applications in laser systems,[25] as optical signal amplifiers,[26] and in fluoroimmunoassay.[10c] Due to the relatively short lifetime of the excited states of the NIR emitting Ln(III) ions, *d*-block complexes having long-lived excited states have been used as sensitizers. While this strategy is being mostly used for sensitizing NIR emitting Ln(III) ions,[27] *d-f* edifices in which the luminescence of the *d*-block partner is enhanced by the intramolecular intermetallic energy transfer from the *f*-counterpart are very rare. Examples of *d-f* edifices in which the *d*-block metal ion is intramolecularly sensitized by lanthanide(III) ions include the triple helical complexes of Eu(III)-Fe(II)[28] and Ln(III)-Cr(III) (Ln = Eu and Tb)[29] reported by Bunzli and his co-workers and the ruthenium(II) bipyridyl complexes containing covalently bound Ln(III) (Ln = Nd, Eu, and Tb) complexes of calixarenes by Beer et al.[30] Terbium(III) and europium(III) luminescent sensors for zinc(II) ion have been reported.[31] In europium(III) and terbium(III) complexes the metal centered emission is due to the $^5D_0 \rightarrow {}^7F_J$ (J = 0-6) and $^5D_4 \rightarrow {}^7F_J$ (J = 6-3) transitions, respectively. Their lowest luminescent MC levels $^5D_0$ (E = ~ 17,200 cm⁻¹) and $^5D_4$ (E = ~ 20,500 cm⁻¹) lie below the lowest energy LC level and upon excitation in the LC bands, intramolecular ligand-to-metal energy transfer can occur and MC luminescence can be observed. The ^{3}MLCT emissive state of Ru^{II}-ttpy complexes (~ 16,200 cm⁻¹)[32] matches with the energy of the $^5D_4$ MC emissive state of terbium(III) (~ 20,500 cm⁻¹). Thus, in *d-f* heterometallic complexes containing terbium(III) and ruthenium(II) the excited states of ruthenium(II) center can be populated by the energy transfer from the excited MC level of terbium(III). Thus, construction of photochemical heterometallic complexes consisting of Ru^{II}-tolylterpyridine complexes covalently appended to terbium(III) complex would improve the luminescence efficiency of the former by the intramolecular

energy transfer from the photoexcited luminescent terbium(III) metal ion. We report herein a Tb^{III}-Ru^{II} heterometallic complex (Chart 1) and the room temperature sensitization of the Ru^{II}(tolylterpyridine) molecular components by the intramolecular energy transfer from the terbium(III) molecular component. We also report the analogues Tb^{III}-Zn^{II} system and demonstrate the role of the terbium(III) complex **2** as a highly selective and zinc(II) ion sensitive luminescent chemosensor.
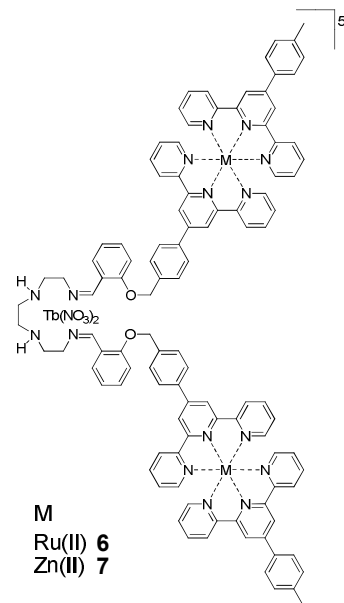

Chart 1. Structure of the *d-f* heterometallic trinuclear supramolecular assemblies $[Tb(NO_3)_2(\mathbf{L^2})\{Ru(ttpy)\}_2](PF_6)_5$ (**6**) and $[Tb(NO_3)_2(\mathbf{L^2})\{(Zn(ttpy)\}_2](NO_3)Cl_4$ (**7**).

Results and Discussion

Synthesis of Organic Precursors and Ligands. 4′-Tolyl-2,2′:6′,2″-terpyridine (ttpy) is synthesized by the one pot synthetic protocol[33,34] based on Hantzsch synthesis (pyridine ring fusion). Bromination of 4′-tolyl-2,2′:6′,2″-terpyridine by *N*-bromosuccinimide in the presence of benzoyl peroxide (initiator) yields 4′-bromomethylphenyl-2,2′:6′,2″-terpyridine (**1**).[33,34] *O*-Alkylation of salicylaldehyde with **1** in ethanol in the presence of sodium hydroxide as proton scavenger gives the tolylterpyridine-appended salicylaldehyde (**L¹**). The Schiff base condensation of triethylenetetraamine with **L¹** in ethanol in a 1:2 mole ratio gives the tolylterpyridine functionalized Schiff base **L²** as yellow needles in 77% yield (Scheme 1).

X-Ray Crystal Structure of L¹. The compound **L¹** (CCDC #708246) crystallizes in the triclinic system with the space group *P* ī and there are two molecules in the asymmetric unit. There is a pseudo mono *C*-face centered unit cell in the crystal lattice which satisfies approximate C_2 space group. Attempts made to solve the structure solution in the C_2 system led to a distorted structure with a residual factor 21%. The molecules and their *C*-translation equivalence are linked through weak C-H···O hydrogen bonds (C28-H28···O1, 0.930 Å, 2.687 Å, 128.9°, symm: x, y, z-1; C50-H50···O3, 0.93 Å, 26.9 Å, 128.5°, symm: x, y, z-1). The terpyridine moiety is planar, whereas the
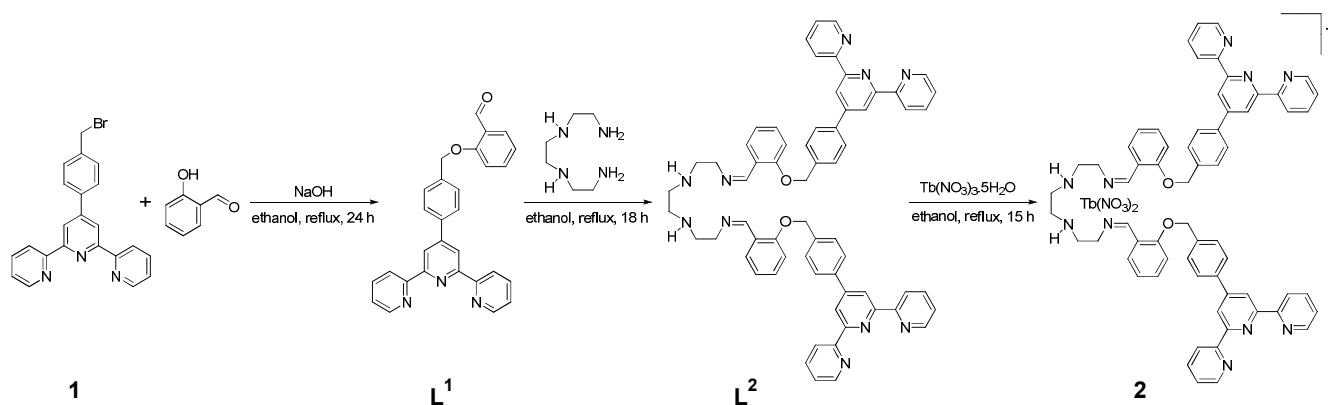
Scheme 1. Synthesis of $\mathbf{L^2}$ and $[\mathrm{Tb(NO_3)_2}(\mathbf{L^2})]\mathrm{NO_3.5H_2O}$ (**2**).

phenyl ring (C38···C43) is inclined to the terpyridine moiety (dihedral angle between the planes 37.40 (8)°). The ORTEP representation of $\mathbf{L^1}$ is presented in Figure 1 and the crystal data are presented in Table 1.
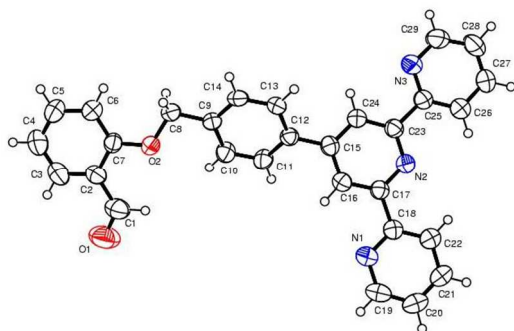

Figure 1. The ORTEP diagram of $\mathbf{L^1}$, thermal ellipsoids are drawn at the 50% probability level (CCDC #708246).

Synthesis of Complexes. The terbium(III) complex $[\mathrm{Tb(NO_3)_2}(\mathbf{L^2})]\mathrm{NO_3.5H_2O}$ (**2**) is synthesized by the Schiff base condensation of triethylenetetraamine with $\mathbf{L^1}$ in the presence of $\mathrm{Tb(NO_3)_3.5H_2O}$ in ethanol (Scheme 1). It is also synthesized by the reaction of the preformed ligand $\mathbf{L^2}$ with $\mathrm{Tb(NO_3)_3.5H_2O}$. Terbium(III) coordinates with the Schiff base compartment of $\mathbf{L^2}$ while the covalently bound tolylterpyridine functionalities remain uncoordinated. The trimetallic heterometallic complex $[\mathrm{Tb(NO_3)_2}(\mathbf{L^2})\{\mathrm{Ru(ttpy)}\}_2](\mathrm{PF_6})_5$ (**6**), containing dinuclear $\mathrm{Ru^{II}}$-ttpy molecular components bridged by the terbium(III) center, is synthesized by the reaction of the preformed terbium(III) complex $[\mathrm{Tb(NO_3)_2}(\mathbf{L^2})]\mathrm{NO_3.5H_2O}$ (**2**) with $[\mathrm{Ru(ttpy)Cl_3}]$ in ethylene glycol-ethanol. The trimetallic assembly $[\mathrm{Tb(NO_3)_2}(\mathbf{L^2})\{\mathrm{Zn(ttpy)}\}_2](\mathrm{NO_3})\mathrm{Cl_4}$ (**7**), consisting of $\mathrm{Zn^{II}}$-ttpy molecular components bridged by the terbium(III) center, is synthesized by the reaction of $[\mathrm{Tb(NO_3)_2}(\mathbf{L^2})]\mathrm{NO_3.5H_2O}$ (**2**) with $[\mathrm{Zn(ttpy)Cl_2}]$ (**3**) in DMF. *d-f* Heterometallic edifices can be constructed by exploiting the thermodynamic differentiation between the *d*- and *f*-metal ions for different set of donor atoms and donor arrays. Lanthanides are known for their preference for Schiff bases,[35] while ruthenium(II) ion prefers polypyridine ligands. The use of the preformed terbium(III) chelate **2** for the synthesis of **6** and **7** ensures their formation as the sole product since the lanthanide cation remains coordinated to the Schiff

Table 1. The crystal data for $\mathbf{L^1}$

description	data
empirical formula	$\mathrm{C_{29}H_{21}N_3O_2}$
formula weight	443.49
color	pale yellow
crystal description	needles
crystal size/mm	0.40 x 0.30 x 0.20 mm
diffractometer	bruker axs kappa apex2 CCD
radiation type	Mo$K\alpha$
crystal system	triclinic
space group	$P\bar{1}$
a/Å	7.074(2)
b/Å	9.8727(4)
c/Å	17.1493(8)
α/deg	81.198(2)
β/deg	89.999(8)
γ/deg	69.007(18)
V/Å^3	1103.1(3)
Z	2
ρ_{calcd}/mg cm^{-3}	1.335
λ/Å	0.71073
T/K	293 (2)
absorption correction	multi-scan
absorption correction range	0.9831-0.9667
2θ range/deg	1.20-24.74
F(000)	464
no. of reflections collected	9227
no. of independent reflections	5725
no. of parameters	622
goodness-of-fit on F^2	1.092
final R indices [$I>2\sigma(I)$]	R1 = 0.0404, wR2 = 0.0971
R^a indices, all data	R1 = 0.0566, ss$w$R2 = 0.1201
largest diff. peak and hole	0.196 and -0.163

^{a} R = $\Sigma\ ||F_o| - |F_c||/\Sigma\ |F_o|$. $R_w = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$.

base compartment and does not compete for the tolylterpyridine moieties. Thus, the use of preformed complexes as ligands and as metals strategy is highly desirable in the construction of multimetallic *d-f* assemblies. The ruthenium(II) complex $[\mathrm{Ru}(\mathbf{L^1})(\mathrm{ttpy})](\mathrm{PF_6})_2$ (**4**) is prepared by the reaction of $\mathbf{L^1}$ with $[\mathrm{Ru(ttpy)Cl_3}]$ in ethylene glycol-ethanol in the presence of *N*-

methylmorpholine. The dinuclear ruthenium(II) complex $[\{Ru(ttpy)\}_2(L^2)](PF_6)_4$ (**5**) is synthesized by the Schiff base condensation of triethylenetetraamine with **4** in ethanol. The ruthenium(II) complexes **4-6** are isolated from the reaction medium as their hexafluorophosphate salts by adding an aqueous solution of potassium hexafluorophosphate. The complexes are stable in solution and in the solid state under ambient conditions. Under the experimental conditions no photochemical decomposition is noticed for any one of the systems reported in the present study.
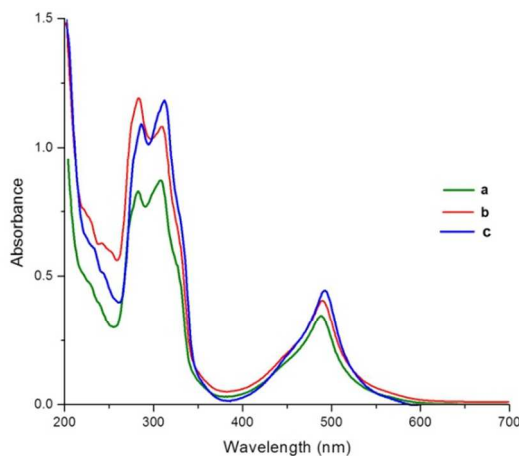

Figure 2. Electronic absorption spectrum of **4** (a), **5** (b), and **6** (c) in acetonitrile at 25 ºC.

Electronic Absorption Spectra. The electronic absorption spectral data of the ligand L^2 and the complexes **2**, **4-7** are presented in Table 2. The free ligand L^2 exhibits three intense absorption bands at 203, 252, and 278 nm (ε = 19,578; 13,627; and 16,233 L mol^{-1} cm^{-1}, respectively) assignable to the π-π^* and n-π^* transitions. The terbium(III) complex $[Tb(NO_3)_2(L^2)]NO_3.5H_2O$ (**2**) exhibits three intense absorption bands at 204, 252, and 278 nm (ε = 17,025; 8,040; and 8,905 L mol^{-1} cm^{-1}, respectively) assignable to the ligand centered (^{1}LC) π-π^* transitions of the coordinated ligand. The complexes $[Ru(L^1)(ttpy)](PF_6)_2$ (**4**) and $[\{Ru(ttpy)\}_2(L^2)](PF_6)_4$ (**5**) exhibit two intense absorption bands at 268-310 nm (ε = 76,200-119,000 L mol^{-1} cm^{-1}) assignable to the ligand centered (^{1}LC) $\pi\rightarrow\pi^*$ transitions of the coordinated ligands and an intense absorption band at 490 nm (ε = 21,000 and 40,200 L mol^{-1} cm^{-1}, respectively) assignable to the ^{1}MLCT ($d_{\pi(Ru)}\rightarrow\pi^*_{(ttpy)}$) transition of the ruthenium(II)(tolylterpyridine) scaffold. The Tb^{III}-Ru^{II} heterometallic complex $[Tb(NO_3)_2(L^2)\{Ru(ttpy)\}_2](PF_6)_5$ (**6**) exhibits two transitions at 284 and 310 nm (ε = 88,500 and 95,800 L mol^{-1} cm^{-1}, respectively) due to the ligand centered (^{1}LC) $\pi\rightarrow\pi^*$ transitions of the coordinated ligands and a broad band at 490 nm (ε = 36,300 L mol^{-1} cm^{-1}) assignable to the ^{1}MLCT ($d_{\pi(Ru)}\rightarrow\pi^*_{(ttpy)}$) transition of the ruthenium(II)(tolylterpyridine) moieties. The Tb^{III}-Zn^{II} heterometallic complex $[Tb(NO_3)_2(L^2)\{Zn(ttpy)\}_2](NO_3)Cl_4$ (**7**) exhibits a transition at 286 nm (ε = 35,727 L mol^{-1} cm^{-1}) assignable to the (^{1}LC) π-π^* transition of the coordinated ligand. Zinc(II), being a d^{10} metal ion, is spectroscopically silent and no d-d transition is observed. The mono- and dinuclear ruthenium(II) complexes **4** and **5** and the Tb^{III}-Ru^{II} d-f heterometallic complex **6** exhibit the ^{1}MLCT ($d_{\pi(Ru)}\rightarrow\pi^*_{(ttpy)}$) transition at 490 nm. The parent

complex $[Ru(ttpy)_2](PF_6)_2$ also exhibits the ^{1}MLCT transition at 490 nm. Ruthenium(II) polypyridine complexes exhibit the ^{1}MLCT transition in the region 490–520 nm.[19a] According to crystal field formalism, low-spin octahedral complexes of ruthenium(II), being a d^6 metal ion, is expected to exhibit two spin allowed crystal field transitions assignable to the $^1A_{1g}\rightarrow^1T_{1g}$ and $^1A_{1g}\rightarrow^1T_{2g}$ transitions in the visible region. However, these transitions are obscured by the relatively intense and broad MLCT transition. The electronic absorption spectra of **4-6** are shown in Figure 2.
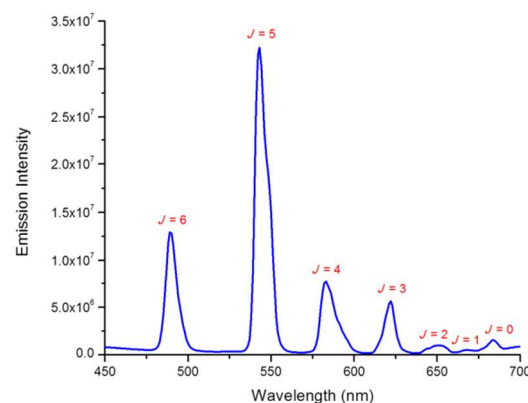

Figure 3. Emission spectrum of $[Tb(NO_3)_2(L^2)](NO_3).5H_2O$ (**2**) (λ_{ex} = 284 nm) in acetonitrile at 25 °C showing the characteristic $^5D_4 \rightarrow {}^7F_J$ transitions of Tb(III).

Luminescence Spectra. The excitation and emission spectral data are presented in Table 2. The excitation spectra of the compounds are monitored at the emission maxima of each compound at 25 °C. The excitation spectrum of the ligand L^2 in acetonitrile shows two intense bands at 267 and 292 nm. Upon excitation it exhibits intense emission bands at 340 and 351 nm. The excitation spectrum of $[Tb(NO_3)_2(L^2)]NO_3.5H_2O$ (**2**) in acetonitrile shows an intense band at 210 nm and two weak bands at 266 and 284 nm. Upon excitation it exhibits emission bands at 490 ($^5D_4\rightarrow^7F_6$), 545 ($^5D_4\rightarrow^7F_5$), 585 ($^5D_4\rightarrow^7F_4$), 622 ($^5D_4\rightarrow^7F_3$), 651 ($^5D_4\rightarrow^7F_2$), 668 ($^5D_4\rightarrow^7F_1$), and 684 ($^5D_4\rightarrow^7F_0$) nm characteristic of the $^5D_4\rightarrow^7F_{0-6}$ emission of terbium(III) metal ion (Figure 3). The excitation spectrum of $[(Ru(ttpy)(L^1)](PF_6)_2$ (**4**) shows a band at 231 nm. Upon excitation it exhibits an emission band at 710 nm. The excitation spectrum of $[\{Ru(ttpy)\}_2(L^2)](PF_6)_4$ (**5**) shows excitation maxima at 230, 257, 280, and 326 nm. Upon excitation it exhibits intense emission bands at 676 and 698 nm. The emission profile and intensity are independent of the excitation wavelength. From the extensive investigations carried out by many research teams, it is well known that light absorption by complexes of ruthenium(II) polypyridine family is generally into the ^{1}MLCT state. Light excitation onto the spin-allowed MLCT band, through excitation of the higher energy LC bands, eventually leads to the population of the lowest energy, usually luminescent, ^{3}MLCT excited state with an efficiency of intersystem crossing assumed to be unity.[17a,d,36]

The excitation spectrum of $[Tb(NO_3)_2(L^2)\{Ru(ttpy)\}_2](PF_6)_5$ (**6**) in acetonitrile shows an intense band at 229 nm and two weak bands at 264 and 284 nm. Upon excitation it exhibits an intense

emission band at 687 nm characteristic of the ruthenium(II)(tolylterpyridine) moieties (Figure 4). The emission profile and position are similar and independent of the excitation wavelength. The excitation spectrum of **6** overlaps with that of the dinuclear ruthenium(II) complex **5**. Upon excitation of **6** at 284 nm it exhibits an emission band at 687 nm characteristic of ruthenium(II) emission. The fluorescence lifetime of **6** in acetonitrile is τ = 1.2 ns which is longer than that of [Ru(ttpy)$_2$]$^{2+}$ (τ = 0.95 ns).[19,37] The Ru^{II}-Tb^{III} *d-f* heterometallic assembly **6** does not exhibit the characteristic $^5D_4 \rightarrow {}^7F_{0-6}$ emission bands of terbium(III) expected in the region 490-622 nm. Since the energy of the $^5D_4$ MC emissive state of the terbium(III) is higher than the energy of the ^{3}MLCT emissive state of the ruthenium(II) center,[38] upon excitation of **6** the terbium(III) molecular component absorbs energy and transfers the electronic energy to the ruthenium(II)(tolylterpyridine) molecular components which results in the population of the ^{3}MLCT state with a concomitant enhancement of the fluorescence lifetime of the latter. The intramolecular intercomponent electronic energy transfer from the terbium(III) to the ruthenium(II) centers makes the *d-f* heterometallic complex **6** luminescent with an increase in lifetime compared to that of [Ru(ttpy)$_2$]$^{2+}$. The room temperature emission band of **6** is red shifted compared to that of [Ru(ttpy)$_2$]$^{2+}$.[19a]
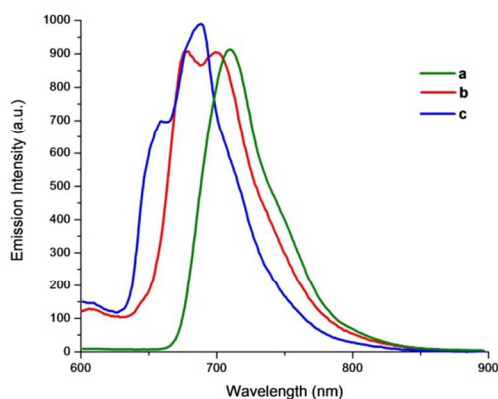

Figure 4. Emission spectrum of **4** (a) (λ_{ex} = 231nm), **5** (b) (λ_{ex} = 280 nm), and **6** (c) (λ_{ex} = 284 nm) in acetonitrile at 25 ºC.

The complex **6** contains ruthenium(II)(tolylterpyridine) and terbium(III) chromophores both of which are potentially luminescent and emission from these two chromophores could, in principle, occur. But, only the ruthenium(II) centered emission at 687 nm is observed indicating that the *f→d* energy transfer is almost quantitative. The *f→d* energy migration process involving europium(III) and terbium(III) is rare due to the high energy of the emitting europium(III) ($^5D_0$) and terbium(III) ($^5D_4$) levels. However, *d→f* energy transfer is common with low energy NIR emitters such as neodymium(III), erbium(III), and ytterbium(III). Forster dipole-dipole mechanism dominates intermetallic *d-f* communications occurring at long distances (> 4 Å) and its efficiency mainly depends on the overlap integral (*J*) between the emission spectrum of the donor and the absorption spectrum of the acceptor.

To ascertain the intramolecular energy transfer from the Tb(III) to the Ru(II) centers in **6**, the Tb^{III}-Zn^{II} analog **7** has been synthesized. Zinc(II), being a d^{10} metal ion, is spectroscopically

silent and the emission of **7** could be solely from the Tb(III) center. The excitation spectrum of [Tb(NO$_3$)$_2$(**L^2**){Zn(ttpy)}$_2$](NO$_3$)Cl$_4$ (**7**) shows an intense band at 288 nm. Upon excitation it exhibits emission bands at 490, 543, 584, 621 and 653 nm assignable to the $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$, $^5D_4 \rightarrow {}^7F_3$ and $^5D_4 \rightarrow {}^7F_2$ transitions, respectively, of Tb(III). Of the seven $^5D_4 \rightarrow {}^7F_{0-6}$ emission bands of terbium(III) the weak bands corresponding to the $^5D_4 \rightarrow {}^7F_{0-1}$ transitions are not observed.[38] Since the Tb^{III}-Zn^{II} system **7** exhibits the characteristic Tb(III) emission, the Tb(III) centre of the Tb^{III}-Ru$^{II}_2$ system **6** is also expected to be emissive and the *f→d* energy transfer accounts for the non-luminescence of the Tb(III) center and the luminescence of the Ru(II) centers. The complex [Zn(bpy)$_3$](PF$_6$)$_2$ exhibits emission at 326 nm which is assigned to the bpy-based fluorescence based on the short-lived (< 10 ns) excited-state lifetime. The emission of [Zn(ttpy)$_2$]$^{2+}$ is also assigned to the metal perturbed π-π* ttpy-based fluorescence.[39] Because zinc(II) is a d^{10} metal ion, this transition does not involve the metal orbitals and is of a triplet ligand-centered (^{3}LC) in nature. The emission of the Tb^{III}-Zn^{II} assembly **7** appears to be the result of the photoinduced intramolecular energy transfer from the coordinated ttpy ligands of the Zn(ttpy)$_2$ molecular components to the Tb(III) $^5D_4$ MC band followed by the $^5D_4 \rightarrow {}^7F_{0-6}$ emissions.[40]

Electrochemistry of Complexes. The redox behavior of the complexes has been investigated in acetonitrile solution to complement the spectroscopic data. The cyclic voltammetric data for the complexes **5-7** are presented in Table 2. The cyclic voltammogram of **5** in acetonitrile in the potential range 0 to 2 V contains an oxidation wave and a reduction wave (E_{pa} = 1 V and E_{pc} = 1.09 V versus Ag/AgCl) corresponding to the Ru(II)/Ru(III) redox process. The ΔE_p value of 0.09 V for the Ru(II)/Ru(III) redox couple indicates that the redox process is irreversible and the $E_{1/2}$ value of 1.04 V indicates that the ruthenium(II) molecular components undergo the metal centered oxidation rather easily when compared to the parent complexes [Ru(tpy)$_2$]$^{2+}$ ($E_{1/2}$ = 1.29 V) and [Ru(ttpy)$_2$]$^{2+}$ ($E_{1/2}$ = 1.24 V).[19a,41] The cyclic voltammogram in the potential region 0 to – 2 V shows a reduction and an oxidation wave (E_{pc} = −1.10 V and E_{pa} = −1.34 V versus Ag/AgCl) due to the reduction of the coordinated tolylterpyridine. The reduction of the coordinated tolylterpyridine takes place in the same potential range as observed for other ruthenium(II) terpyridine complexes.[19a,41] The ΔE_p value of 0.24 V indicates that the ligand centered redox process is quasireversible and the $E_{1/2}$ value of −1.22 V (versus Ag/AgCl) is very close to that of [Ru(ttpy)$_2$]$^{2+}$ ($E_{1/2}$ = −1.24 V).[19a] The cyclic voltammogram of **6** in acetonitrile in the potential range 0 to 1.30 V contains an oxidation and a reduction wave (E_{pa} = 0.98 V and E_{pc} = 0.87 V versus Ag/AgCl) for the Ru(II)/Ru(III) redox process. The ΔE_p value of 0.10 V for the Ru(II)/Ru(III) redox couple indicates that the redox process is irreversible and the $E_{1/2}$ value of 0.93 V indicates that the ruthenium(II) molecular components undergo the metal centered oxidation easily when compared to the parent complexes [Ru(tpy)$_2$]$^{2+}$ ($E_{1/2}$ = 1.29 V) and [Ru(ttpy)$_2$]$^{2+}$ ($E_{1/2}$ = 1.25 V).[37,41] The cyclic voltammogram of **6** in the potential range 0.0 to −2 V shows two ligand centered redox processes and the ΔE_p values indicate that these redox processes are quasireversible. The complex [Tb(NO$_3$)$_2$(**L^2**){(Zn(ttpy)}$_2$](NO$_3$)Cl$_4$ (**7**) exhibits a ligand centered reduction and the $E_{1/2}$ vaule for the redox couple is -1.31 V (versus Ag/AgCl) in acetonitrile.

Conclusions

The *d-f* heterometallic complexes [Tb(NO$_3$)$_2$(**L^2**){Ru(ttpy)}$_2$]-(PF$_6$)$_5$ (**6**) and [Tb(NO$_3$)$_2$(**L^2**){Zn(ttpy)}$_2$](NO$_3$)Cl$_4$ (**7**) consisting of ruthenium(II)/zinc(II)(tolylterpyridine) molecular components covalently appended onto the periphery of terbium(III) Schiff base chelate have been synthesized by employing the strategy of complexes as metals and as ligands. The synthetic methodologies developed in this study would enable the construction of new polymetallic *d-f* systems. The Tb^{III}–Ru^{II} heterometallic complex **6** is luminescent at room temperature in fluid solution and exhibits absorption-energy transfer-emission (A-ET-E) process characteristic of light conversion molecular devices. The present study demonstrates the feasibility of synthesizing Tb^{III}-Ru^{II} heterometallic complexes for studying intercomponent intramolecular *f→d* energy transfer process. The lanthanide(III)-centered excited states are located below ~ 20,000 cm^{-1} (except for Gd) which are amenable to undergo significant overlap with the broad *d-d* or CT bands of the *d*-block chromophores. The energy of the MLCT states of transition metal ions largely depends on the coordination environment and can, therefore, be tuned by modifying the hosting ligands. Thus, it is possible to control the energy migration pathway, i.e., the lanthanide sensitized *d*-metal ion luminescence (*f→d* energy transfer) or the *d*-metal sensitized lanthanide luminescence (*d→f* energy transfer) in *d-f* heterometallic complexes.

Experimental

Materials. 2-Acetylpyridine, ruthenium(III) chloride trihydrate, *p*-tolualdehyde, and terbium(III) nitrate pentahydrate (Aldrich); zinc chloride, salicylaldehyde, triethylenetetramine, ammonium acetate, potassium carbonate, acetamide, and potassium hexafluorophosphate (Fluka); ethylene glycol, hydrogen peroxide, ammonium iron(II) sulfate hexahydrate, and *N*-methylmorpholine (Merck) were used as received. DMF, methanol, ethanol, and acetonitrile were purified by the literature methods.[42] HPLC grade acetonitrile and DMF (Merck) were used for spectroscopic and photophysical studies. 4′-Tolyl-2,2′:6′,2″-terpyridine,[33] 4′-(*p*-bromomethylphenyl)-2,2′:6′,2″-terpyridine (**1**),[33] and [Ru(ttpy)Cl$_3$][43] were prepared according to the published procedures.

Physical Measurements. Buchi rotavapor (Model R-124) along with Buchi V-700 vacuum pump and V-850 controller was used to remove the solvent and isolate the products at low temperature and pressure. CHN microanalyses were carried out using Perkin-Elmer 2400 Series II CHNS/O Elemental Analyzer interfaced with a Perkin-Elmer AD 6 Autobalance. Helium (analytical grade) was used as the carrier gas. Infrared spectra were recorded on a Perkin-Elmer Spectrum RX-I FT-IR spectrometer in the range 4000-400 cm^{-1} using KBr pellets. ^{1}H NMR spectra were recorded in CDCl$_3$ (99.95 atom %D, Aldrich) on Jeol GSX 400 MHz multinuclear NMR spectrometer at 25 °C using standard 5 mm probe. FAB mass spectra were recorded on a JEOL SX 102/Da-600 Mass spectrometer/data system using argon/xenon (6 kV, 10 mA) as the FAB gas. *m*-Nitrobenzyl alcohol (NBA) was used as the matrix. Electrospray ionization mass spectra were recorded using Micromass Quattro-II Triple Quatrupole Mass spectrometer. MALDI-TOF mass spectra were recorded on Applied Biosystems Voyager System 6316 using *α*-cyanocinnamic acid as the matrix.

X-ray diffraction studies were carried out using Bruker axs kappa Apex II single crystal X-ray diffractometer equipped

with graphite monochromated Mo(K*α*) (λ = 0.7107 Å) radiation and CCD detector. The electronic absorption spectra were recorded on a Perkin-Elmer Lambda 25 UV-Visible spectrophotometer controlled by the WinLab software through a computer. The spectra were recorded in the region 190-900 nm in acetonitrile at 25 ºC using a matched pair of Teflon stoppered quartz cell of path length 1 cm. Fluorescence spectra were recorded on a Fluorolog-3 FL3-221 spectrofluorometer. The excitation source was a 450 W CW Xenon lamp. The band pass for the excitation and double-grating emission monochromator was set at 2 nm. A quartz cell of path length 10 mm was used. All emission spectra were corrected for the instrumental function. All photophysical studies and measurements were made in deoxygenated acetonitrile (HPLC grade) by purging argon at 25 °C. Fluorescence lifetime measurements were carried out using the time correlated single photon counting technique (TCSPC) with microchannel plate photomultiplier tube (MCP-PMT) as detector and picosecond laser as the excitation source. The fluorescence lifetime is obtained by deconvoluting the excitation and instrument response function from the measured fluorescence decay. The data analysis was carried out by the IBH DAS-6 software which is based on reconvolution technique using iterative nonlinear least square methods.

Cyclic voltammetry was performed on a EG&G PAR 273A Potentiostat/Galvanostat using RDE0018 Analytical Cell Kit consisting of thermostated cell bottom, EG&G G0229 glassy carbon disk milli-electrode, platinum counter electrode, and EG&G K0265 Ag/Ag$^+$ reference electrode. The auxiliary electrode was connected to the test solution through the counter electrode bridge tube. The reference electrode was separated from the test solution through the bridge tube containing AgCl-KCl filling solution. Cyclic voltammograms were recorded using 10^{-3} M solution of the complexes in oxygen free acetonitrile containing 0.1 M tetraethylammonium perchlorate as the supporting electrolyte. Oxygen free argon, saturated with the solvent vapor, was flushed through each sample solution through the purge tube assembly for 30 min before voltammetry was performed and all measurements were carried out in an atmosphere of argon at 25 ºC. All operations were performed through a computer using EG&G Model 270 software and all electrochemical parameters were obtained using the EG&G PowerSuite software (version 2.58). The instrument was calibrated by recording the cyclic voltammogram of ferrocene (purum, Fluka) in oxygen free acetonitrile under the same experimental conditions.

Synthesis of Ligands

2-(4-(2,2′:6′,2″-Terpyridin-4′-yl-benzyloxy)benzaldehyde (L^1).

To a suspension of salicylaldehyde (0.49 g, 4 mmol) and sodium hydroxide (0.16 g, 4 mmol) in dry ethanol (100 mL) was added 4′-(*p*-bromomethylphenyl)-2,2′:6′,2″-terpyridine (1.61 g, 4 mmol) in dry ethanol (30 mL) dropwise for 30 min, refluxed under argon atmosphere for 24 h, and cooled to room temperature. The solid particles that separated out were filtered off and the filtrate was flash evaporated to dryness. The resulting solid product was dissolved in chloroform (50 mL) and washed thoroughly with water (50 mL) to remove the excess base and sodium bromide which was formed as the side product. The organic layer was dried over sodium sulfate, filtered, the filtrate was flash evaporated to get a pale yellow solid, and recrystallized in chloroform. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a solution of L^1 in chloroform-methanol (1:1 v/v) at room temperature (1.24 g, 70%). mp 218 °C. Found: C, 78.52; H, 4.72; N, 9.44. Calc. for

$C_{29}H_{21}N_3O_2$: C, 78.54; H, 4.77; N, 9.47%. ν_{max}/cm^{-1} 3061 ν(C–H) (aromatic), 2969 ν(C–H) (aliphatic), 2849 ν(C–H) (aldehyde), 1688 ν(C=O), 1599 ν(C=N), 1387 δ(C–H) (aldehyde), 1244 ν_{as}(C–O–C), 1038 ν_s(C–O–C). δ_H(500 MHz; CDCl$_3$; 298 K) 5.26 (2 H, s, -CH$_2$-); 7.05 (1H, d, J = 9.5 Hz), 7.36 (1H, t, J = 3.7 Hz), 7.57 (1H, t, J = 5.25 Hz), 7.93 (1H, d, J = 6.5 Hz), 7.15 (4H, d, J = 8.0 Hz), 7.86 (2H, d, J = 6.0 Hz), 7.53 (2H, t, J = 4.25 Hz), 7.88 (2H, t, J = 7.5 Hz), 7.95 (2H, d, J = 6.5 Hz), 8.67 (2H, d, J = 7.9 Hz), 10.51 (s, 1 H, -CHO). δ_C(125 MHz; CDCl$_3$; 298 K) 70.1, 113.0, 118.8, 121.1, 121.3, 123.2, 123.8, 127.7, 135.7, 138.5, 149.1, 149.6, 156.0, 156.1, 160.9, 189.0. FAB MS: m/z 444 [M]$^+$, 323 [M–C$_7$H$_5$O$_2$]$^+$, 223 [M–C$_{14}$H$_{10}$N$_3$]$^+$.

N^1,N^2-Bis(2-((Z)-2-(4-(2,2′:6′,2″)-terpyridin-4′-yl-benzyloxy)benzylideneamino)ethyl)ethane-1,2-diamine (L^2).

To a solution of triethylenetetraamine (0.75 mL, 5.12 mmol) in dry ethanol (150 mL) was added 2-(4-(2,2′:6′,2″)-terpyridin-4′-yl-benzyloxy)benzaldehyde (L^1) (4.59 g, 10.34 mmol) in ethanol (200 mL) dropwise over a period of 1 h and refluxed under stirring for 18 h. The yellow solution was flash evaporated and the resulting yellow powder was purified by column chromatography by eluting with ethyl acetate-ethanol (1:1 v/v). The first fraction was collected and allowed to stand at room temperature overnight whereupon yellow needles separated out (4 g, 77%). mp 116 °C. Found: C, 77.00; H, 5.54; N, 13.90. Calc. for $C_{64}H_{56}N_{10}O_2$: C, 77.08; H, 5.66; N, 14.05%. ν_{max}/cm^{-1} 3403 ν(N–H), 3053 ν(C–H) (aromatic), 2975 ν(C–H) (aliphatic), 1651 ν(C=N), 1584 ν(C–H) (pyridine), 1387 δ(C–H), 791 δ(C–H) (aliphatic). δ_H(500 MHz; CDCl$_3$; 298 K) 1.30 (m, 8H, -^{a}CH$_2$-NH-^{c}CH$_2$-CH$_2$-N=), 2.45 (s, 2H, -CH$_2$-^{b}NH-CH$_2$-CH$_2$-N=), 3.60 (m, 4H, -NH-CH$_2$-^{d}CH$_2$-N=), 4.61 (s, 4H, -O-^{j}CH$_2$-C$_6$H$_4$-), 7.05 (m, 4H, ^{g,i}H), 7.34 (s, 4H, ^{p}H), 7.50 (m, 2H, ^{h}H), 7.52 (s, 4H, ^{l}H), 7.90 (m, 2H, ^{f}H), 7.93 (m, 8H, ^{k}H, ^{o}H), 8.68 (m, 6H, -N=^{e}CH-C$_6$H$_4$-, ^{q}H), 8.70 (s, 4H, ^{n}H), and 8.75 (s, 4H, ^{m}H). δ_C(125 MHz; CDCl$_3$; 298 K) 42.1, 49.2, 52.3, 72.3, 118.7, 118.8, 121.4, 123.8, 125.2, 127.3, 127.4, 128.1, 129.6, 135.9, 136.8, 137.6, 149.1, 150.0, 155.9, 156.1, 156.3, 159.7. ESI MS: m/z 998 [M+H]$^+$, 572 [(M–L^1+2H]$^+$, 346 [tpy+Na]$^+$, 324 [ttpy+H]$^+$.

Synthesis of Complexes

[Tb(NO$_3$)$_2$(L^2)]NO$_3$.5H$_2$O (2), *Method 1*. To a solution of triethylenetetraamine (0.37 g, 2.50 mmol) in dry ethanol (50 mL) was added L^1 (2.22 g, 5 mmol) in dry ethanol (100 mL) dropwise for 10 min and heated to 60 ºC. Terbium(III) nitrate pentahydrate (1.09 g, 2.5 mmol) in ethanol (20 mL) was added dropwise and refluxed for 24 h under argon atmosphere. The pale yellow solid that separated out was recrystallized in ethanol and dried in vacuo (1.07 g, 30%). *Method 2*. A solution of L^2 (1.60 g, 1.60 mmol) in ethanol (60 mL) was added to a solution of Tb(NO$_3$)$_3$.5H$_2$O (0.70 g, 2.08 mmol) in ethanol (100 mL) under stirring and refluxed for 15 h. The resulting yellow solution was flash evaporated to dryness and the pale yellow solid was recrystallized in ethanol (0.58 g, 25%). Found: C, 53.62; H, 4.60; N, 12.69. Calc. for $C_{64}H_{66}N_{13}O_{16}$Tb: C, 53.67; H, 4.65; N, 12.72%. ν_{max}/cm^{-1} 3433 ν(N–H), 3051 ν(C–H) (aromatic), 2950 ν(C–H) (aliphatic), 1635 ν(C=N), 1584 ν(C–H) (pyridine), 1467 ν(N=O), 1242 ν_{as}(NO$_2$), 1038 ν_s(NO$_2$), 1383 ν(N–O). MALDI-TOF MS: m/z 1431 [M–H]$^+$, 1105 [(M–(ttpy+4)]$^+$, 648 [M–(NO$_3$)$_2$]$^{2+}$.

[Zn(ttpy)Cl$_2$] (3). To a solution of ZnCl$_2$ (0.85 g, 6.19 mmol) in ethanol (50 mL) was added a solution of 4-tolyl-2,2′:6′,2″-terpyridine (2 g, 6.19 mmol) in ethanol (100 mL) dropwise and

the resulting solution was refluxed for 4 h with stirring whereupon a colorless spongy product was formed. The reaction mixture was cooled to room temperature and the colorless solid was filtered through Whatman filter paper, washed with ethanol, and dried in vacuum overnight (1.96 g, 71%). Found: C, 56.20; H, 3.65; N, 8.87. Calc. for $C_{22}H_{17}Cl_2N_3Zn$: C, 57.48; H, 3.73; N, 9.14%. ν_{max}/cm^{-1} 3058 ν(C-H) (aromatic), 2919 ν(C-H) (aliphatic), 1601 ν(C=N), 1573 ν(C-H) (pyridine), 1402 ν(C-C) (phenyl), 793 δ(C-H) (aliphatic). ESI MS: m/z 459 [M]$^+$, 424 [(M–Cl]$^+$.

[Ru(ttpy)(L^1)](PF$_6$)$_2$ (4). To a solution of L^1 (0.89 g, 2 mmol) in ethylene glycol-ethanol (1:1 v/v, 30 mL) was added [Ru(ttpy)Cl$_3$] (1.06 g, 2 mmol) in ethylene glycol (50 mL) and refluxed in the presence of N-methylmorpholine (2 drops) for 18 h under argon atmosphere. An aqueous solution of potassium hexafluorophosphate was added and the orange red solid that separated out was filtered, washed with water, and dried in air. Found: C, 52.85; H, 3.29; N, 7.23. Calc. for $C_{51}H_{38}F_{12}N_6O_2P_2Ru$: C, 52.90; H, 3.31; N, 7.26%. ν_{max}/cm^{-1} 2923 ν(C–H) (aliphatic), 788 δ(C–H) (aliphatic), 1685 ν(C=O), 1406 ν(C–C) (phenyl), 845 and 558 ν(P–F). ESI MS: m/z 1013 [M–PF$_6$]$^+$, 434 [M–2PF$_6$]$^{2+}$.

[{Ru(ttpy)}$_2$(L^2)](PF$_6$)$_4$ (5). A solution of [Ru(ttpy)(L^1)](PF$_6$)$_2$ (4) (0.58 g, 0.50 mmol) in ethanol (60 mL) was added triethylenetetraamine (0.04 g, 0.25 mmol) in ethanol (25 mL) and refluxed under argon atmosphere for 6 h. The solution was flash evaporated to half of its volume, an aqueous solution of potassium hexafluorophosphate was added, and the reddish orange solid that separated out was filtered, washed with ethanol followed by diethyl ether, and dried in vacuo. Found: C, 53.41; H, 3.72; N, 9.21. Calc. for $C_{108}H_{90}F_{24}N_{16}O_2P_4Ru_2$: C, 53.47; H, 3.74; N, 9.24. ν_{max}/cm^{-1} 3392 ν(N–H), 2930 ν(C–H) (aliphatic), 788 δ(C–H), 1607 ν(C=N), 1246 ν(C–O), 1085 ν(C–O) (phenolic), 1405 ν(C–C) (phenyl), 838 and 557 ν(P–F). ESI MS: m/z 1078 [M–2PF$_6$]$^{2+}$, 679 [M–3PF$_6$]$^{3+}$, 464 [(M+3)–4PF$_6$]$^{4+}$, 374 [Ru(ttpy)$_2$]$^{2+}$.

[Tb(NO$_3$)$_2$(L^2){Ru(ttpy)}$_2$](PF$_6$)$_5$ (6). To a solution of [Tb(NO$_3$)$_2$(L^2)]NO$_3$.5H$_2$O (2) (0.72 g, 0.5 mmol) in ethylene glycol-ethanol (1:1 v/v, 30 mL) was added [Ru(ttpy)Cl$_3$] (0.53 g, 1 mmol) in ethylene glycol (20 mL) followed by N-methylmorpholine (2 drops), and refluxed for 12 h with stirring under argon atmosphere. An aqueous solution of potassium hexafluorophosphate was added and the reddish orange solid that separated out was filtered, washed with water, and dried in air (0.57 g, 40%). Found: C, 45.41; H, 3.08; N, 8.80. Calc. for $C_{108}H_{90}F_{30}N_{18}O_8P_5Ru_2Tb$: C, 45.45; H, 3.18; N, 8.83. ν_{max}/cm^{-1} 3423 ν(N–H), 2925 ν(C–H) (aliphatic), 1606 ν(C–O), 1406 ν(C–C) (phenyl), 788 δ(C–H) (aliphatic), 1478 ν(N=O), 1245 ν_{as}(NO$_2$), 1028 ν_s(NO$_2$), 840 and 558 ν(P–F). MALDI-TOF MS: m/z 429 [(M–5PF$_6$)+H$_2$O]$^{5+}$, 805 [M–3PF$_6$]$^{3+}$, 567 [(M–2H)–4PF$_6$]$^{4+}$, 747 [Ru(ttpy)$_2$]$^+$, 374 [Ru(ttpy)$_2$]$^{2+}$.

[Tb(NO$_3$)$_2$(L^2){(Zn(ttpy)}$_2$](NO$_3$)Cl$_4$ (7). A solution of [Zn(ttpy)Cl$_2$] (3) (0.40 g, 0.83 mmol) in DMF (100 mL) was added to a solution of [Tb(NO$_3$)$_2$(L^2)]NO$_3$.5H$_2$O (2) (0.56 g, 0.42 mmol) in DMF (100 mL) under stirring and refluxed for 6 h. The solution was flash evaporated to half its volume and the resulting solution was allowed to stand at room temperature for 3 days whereupon colorless transparent crystals separated out. The crystals were filtered and used without further purification (0.35 g, 37%). Found: C, 57.19; H, 3.88; N, 11.59. Calc. for $C_{108}H_{90}Cl_4N_{19}O_{11}TbZn_2$: C, 57.36; H, 4.01; N, 11.77. ν_{max}/cm^{-1} 3473 ν(N-H), 3060 ν(C-H) (aromatic), 2919 ν(C-H) (aliphatic),

1600 ν(C-O), 1402 ν(C-H) (phenyl), 791 δ(C-H) (aliphatic), 1475 ν(N=O), 1252 ν_{as}(NO$_2$), 1014 ν_s(NO$_2$). ESI MS: *m/z* 2264 [M+2H]$^+$, 1506 [{M–(Zn(ttpy))$_2$}+H$_2$O]$^+$, 324 [ttpy+H]$^+$.

Acknowledgements

Notes and references

1 For a broad overview of the discovery and resources of rare earths and their use in advanced materials and technologies, see, ref 1a. For a review on lanthanide-based luminescent hybrid materials, see, ref 1b. For a review on a wide range of applications of the luminescent lanthanide ions, see, ref 1c. For an overview of synthetic methods for mono- and polymetallic edifices exhibiting fascinating optical and magnetic properties, see, ref 1d. (a) S. V. Eliseeva and J.-C. G. Bunzli, *New J. Chem.*, 2011, **35**, 1165-1176. (b) K. Binnemans, *Chem. Rev.*, 2009, **109**, 4283-4374. (c) J.-C. G. Bunzli and C. Piguet, *Chem. Soc. Rev.*, 2005, **34**, 1048-1077. (d) J.-C. G. Bunzli, *Acc. Chem. Res.*, 2006, **39**, 53-61.

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Table 2. Photophysical[a] and electrochemical[b] data of the complexes

compound	entry no.	absorption λ_{max} (nm) ($\varepsilon \times 10^4$, L mol^{-1} cm^{-1})	excitation λ_{ex} (nm)	emission λ_{em} (nm)	metal centered oxidation (V)		ligand centered reductions (V)	
					$E_{1/2}$	ΔE_p	$E_{1/2}$	ΔE_p
L^2		203 (1.95) 252 (1.36) 278 (1.62)	267 292	340, 351				
[Tb(NO$_3$)$_2$(**L^2**)]NO$_3$.5H$_2$O	**2**	204 (1.70) 252 (0.80) 278 (0.89)	210 266 284	490, 545, 585, 622, 651, 668, 684				
[(Ru(ttpy) (**L^1**)](PF$_6$)$_2$	**4**	268 (9.80) 310 (7.69) 490 (2.10)	231	710				
[{Ru(ttpy)}$_2$(**L^2**)](PF$_6$)$_4$	**5**	283 (12.0) 309 (10.9) 490 (4.02)	230 257 280 326	676, 698	1.04	0.09	−1.22	0.24
[Tb(NO$_3$)$_2$(**L^2**){Ru(ttpy)}$_2$](PF$_6$)$_5$	**6**	284 (8.85) 310 (9.58) 490 (3.63)	229 264 284	687	0.93	0.10	−1.24, −1.73	0.31
[Tb(NO$_3$)$_2$(**L^2**){(Zn(ttpy)}$_2$](NO$_3$)Cl$_4$	**7**	286 (3.57)	288	490, 543, 584, 621, 653			−1.31	

[a] Absorption and emission spectra were recorded using 10^{-5} M solution of the complexes in acetonitrile at 298 K.
[b] The data were computed from the cyclic voltammograms recorded on a glassy carbon millielectrode in acetonitrile (10^{-3} M) using tetraethylammonium perchlorate as the supporting electrolyte (0.1 M) at 298 K at the scan rate of 50 mV s^{-1}. Potentials are reported in volt versus Ag/Ag$^+$.

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