# **Inorganic Chemistry**

### Luminescence Tunable Europium and Samarium Complexes: Reversible On/Off Switching and White-Light Emission

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ABSTRACT: Single-molecule functional materials with luminescence tunable by external stimuli are of increasing interest due to their application in sensors, display devices, biomarkers, and switches. Herein, new europium and samarium complexes with ligands having triphenylamine (TPA) groups as the redox center and 2,2'-bipyridine (bpy) as the coordinating groups and diketonate (tta) as the second ligand have been constructed. The complexes show white-light emission in selected solvents for proper mixtures of the emission from Ln<sup>3+</sup> ions and the ligands. Meanwhile, they exhibit reversible luminescence switching on/off properties by controlling the external potential owing to intramolecular energy transfer from the Ln<sup>3+</sup> ions to the electrochemically generated radical cation of **TPA**<sup>•+</sup>. Time-dependent density functional theory (TD-DFT) calculations have been performed to study the electronic spectra. The proposed intramolecular energy transfer processes have been verified by density functional theory (DFT) studies.



#### ■ INTRODUCTION

Single-molecule functional materials with luminescence tunable by external stimuli, e.g. heat,<sup>1</sup> pH,<sup>2</sup> light,<sup>3</sup> electrons,<sup>4</sup> and others,<sup>5</sup> have been widely studied as sensors, display devices, biomarkers, and so on. Electrofluorochromic behavior was proposed by Lehn and co-workers in 1993,<sup>6</sup> which means that one material shows both electrochromic properties and fluorescence. In principle, this kind of molecule may exhibit tunable luminescence by electronic triggering. One of the strategies to build up this kind of molecule is choosing suitable fluorophores and redox-active electrochromic organic groups to construct dyads, in which the intrinsic electron transfer or energy transfer will be changed by external electronic stimuli. The typical fluorophores are naphthalimide, dansyl, and ruthenium complexes and the redox-active electrochromic organic groups may be triphenylamine, tetrazine, quinones, tetrathiafulvalenes, and macrocycles containing metals.

Luminescent lanthanide complexes have inspired researchers' interest in recent decades due to their various photoluminescence properties and their optical applications such as amplifiers,<sup>8</sup> laser materials,<sup>9</sup> organic light-emitting diodes (OLEDs),<sup>10</sup> metal ion detection,<sup>11</sup> cancer diagnosis,<sup>12</sup> therapy,<sup>13</sup> and luminescent thermometers.<sup>14</sup> In addition, luminescent lanthanide ions (e.g., Eu<sup>3+</sup>, Tb<sup>3+</sup>, Sm<sup>3+</sup>, Yb<sup>3+</sup>, Nd<sup>3+</sup>, Er<sup>3+</sup>) in visible or/and near-infrared (NIR) regions have long excited-state lifetimes and narrow emission bands, and they can be promising candidates as fluorophores to construct dyads with electrofluorochromic properties. So far, electrofluorochromic molecules based on luminescent lanthanide complexes have rarely been reported.<sup>15–17</sup> The Rigaut group reported ytterbium and ruthenium d-f heterobimetallic carbon-rich complexes, and the NIR luminescence of Yb was controlled by the redox of the Ru moiety.<sup>15</sup> Yano and coworkers have reported a Eu compound with a terpyridinetriphenylamine redox ligand, showing on/off luminescence switching properties, and they considered the energy transfer from a diketonate moiety to a triarylamine radical cation as the intrinsic reason for emission quenching.<sup>16</sup> All of these lanthanide complexes are made from one redox-active moiety and a lanthanide fluorophore. It seems desirable to seek novel lanthanide molecules with electrofluorochromic properties, to study their optical properties and understand their intramolecular energy transfer processes and further to explore their various applications in white-light materials, molecular switches, ion detection, and so on.

Triphenylamine (TPA) and its derivatives are known as electrochromic materials showing different absorption spectra

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Scheme 1. Molecular Structures of the Ligands TPA-bpy (L1) and TPA-xy-bpy (L2) and Complexes 1-3



in their different redox states. They are used in optical displays or organic solar cells for their excellent photophysical properties.<sup>18</sup> Recently, Lin et al. reported triphenylamine derivatives with aggregation-induced emission (AIE) active pendant groups having remarkable electrofluorochromic behaviors.<sup>19</sup> Cai et al. studied a series of polymers with pyrrole and triarylamine units and found that they had excellent stability for electrofluorochromic properties.<sup>20</sup> Meanwhile, some molecules containing organic ligands with amine derivative moieties and lanthanide ions exhibit white-light emission,<sup>21</sup> and proper mixtures of the emission from organic ligands and lanthanide ions produce white light under some conditions. These single-component white-light emitters have more advantages in generating white light than the traditional method by physical mixing of two (blue/yellow) or three (red/ blue/green) separate emitters. It is considered that they may simplify the preparation of lighting and display devices. Furthermore, they may avoid the drawbacks of separate emitters such as degradation at different rates, having different requirements in device production.<sup>21</sup>

Eu<sup>3+</sup> and Sm<sup>3+</sup> complexes have been well explored for their emission in the visible range, though Sm3+ also has NIR emission. It is particularly interesting that the absorption band of the TPA group in its one-electron-oxidized form lies in the visible-NIR range (~750 nm).<sup>22</sup> Thus, with TPA groups and Eu<sup>3+</sup> or Sm<sup>3+</sup> emitters, we anticipated molecules exhibiting luminescence on/off switching as well as electrochromic properties by controlling the redox states of the TPA units. Furthermore, additional organic chromophores should be included to sensitize Ln<sup>3+</sup> ions except for the redox-active electrochromic ligand, because lanthanide ions with low absorption coefficients are difficult to excite due to the Laporte-forbidden 4f-4f transitions.  $\beta$ -Diketones and their derivatives are among the most popular ligands acting as "antennas" to harvest light and sensitize Ln3+ ions, because of their high thermal and chemical stability as well as their strong ability to coordinate to Ln<sup>3+</sup> ions.<sup>23</sup> To improve the luminescence behavior of lanthanide complexes, C-H bonds

of the organic ligands are considered to be replaced by C–F bonds, because the C–H, O–H, and N–H bonds with highenergy oscillators may decrease the emission intensity of  $Ln^{3+}$  ions.<sup>24</sup> For example, thenoyltrifluoroacetone (Htta) is a good candidate to sensitize  $Ln^{3+}$  ions such as  $Eu^{3+}$ ,  $Sm^{3+}$ , and  $Yb^{3+}$  ions.

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On the basis of the consideration that we mentioned above, the two new ligands  $L_1$  (TPA-bpy) and  $L_2$  (TPA-xy-bpy) (xy = xylene) containing a triphenylamine (TPA) moiety as the redox center and 2,2'-bipyridine (bpy) as the coordinating group have been designed, synthesized, and coordinated to  $Ln(tta)_3 \cdot 2H_2O$  (Ln = Eu<sup>3+</sup>, Sm<sup>3+</sup>, Htta = 2-thenoyltrifluoroacetone)<sup>25</sup> to prepare the complexes  $Ln(L)(tta)_3$  (L = L<sub>1</sub>, Ln = Eu (1), Sm (2); L = L<sub>2</sub>, Ln = Eu (3)) (Scheme 1). These new ligands and complexes have been characterized by <sup>1</sup>H NMR spectroscopy, mass spectroscopy, elemental analyses, and infrared (IR) spectroscopy. Single crystals of the ligand  $L_1$ and complexes 1 and 2 suitable for X-ray single-crystal diffraction were obtained in dichloromethane/ethanol solution and the structures have been determined. The UV-vis absorption and photoluminescence properties of the ligands and complexes have been investigated systemically in various solvents and also in the solid state. Interestingly, white-light emission is observed for 1-3 according to the 1931 CIE (International Commission on Illumination) coordinate diagram. Radiative  $(k_r)$  and nonradiative rate constants  $(k_{nr})$ have been determined from the emission lifetime  $\tau_{\rm obs}$  and emission quantum yield measurements. Complexes 1 and 2 show good luminescence switching properties upon application of an electrochemical potential. In addition, density functional theory (DFT) calculations have been carried out to study the photophysical properties of the ligands and complexes, in order to further understand the energy transfer processes.



Figure 1. (a) X-ray crystal structure of the ligand  $L_1$  (50% probability ellipsoids, H atoms omitted for clarity). (b) Intermolecular  $\pi \cdots \pi$  and CH $\cdots \pi$  noncovalent interactions between the nearest neighbors of  $L_1$ . Color code: blue for N, gray for C, red for O.

#### EXPERIMENTAL

Materials and Instruments. All of the starting materials (A.R. grade) and the dry solvents (THF >99.9%, DCM >99.9%, CH<sub>3</sub>CN >99.8%) were purchased from commercial sources and used directly without any purification. <sup>1</sup>H NMR spectra were measured on a Bruker Avance III instrument operating at 400 MHz frequency. Elemental analysis of C, H, and N was done with an Elementar Vari EL Cube instrument. Mass spectra were recorded on a DECAX-30000 LCQ Deca XP instrument (70 eV). The FTIR spectra were performed on a Thermo Nicolet is50 instrument, with KBr disks in the 525-4000 cm<sup>-1</sup> region. Cyclic voltammetry was performed with three electrodes (working electrode, Pt electrode; reference and counter electrodes, Ag wire) on a Princeton PARSTAT MC instrument. Dry CH<sub>3</sub>CN with 0.1 or 0.25 M tetra-nbutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) was used as a supporting electrolyte solution for the electrochemistry and spectroelectrochemistry measurements. The redox potential values were calibrated by using small amounts of ferrocene as an internal reference. Spectroelectrochemistry was performed with a Pt-grid electrode and two Ag wires in a thin-layer cuvette. Optical absorption spectroscopy was done on a Cary 5000 UV-vis-NIR spectrophotometer from Agilent. Steadystate luminescence was measured on an FLS980 apparatus from Edinburgh Instruments or an Ocean Optics QE65PRO

and HR4000 fiber optic spectrometer. Luminescence decays were measured on an LPS980 spectrometer from Edinburgh Instruments, using an OPO laser (NT242-1K-SH/SFG-SCU-H/2H, EKSPLA) for excitation with a pulse repetition rate of 1 kHz and excitation pulse lengths of 4-7 ns. The photoluminescence quantum yields were measured by a HORIBA Jobin-Yvon FluoroMax-4 spectrometer equipped with an integrating sphere. X-ray single-crystal diffraction data were collected with a Bruker D8 Venture diffractometer. The initial structure was solved by direct methods with the SHELX and Olex2 programs and then refined by full-matrix least squares on  $F^{2,26}$  All of the crystal structures have been deposited with the Cambridge Crystallographic Database (CCDC) with file numbers 1946992 (L<sub>1</sub>), 1946995 (1), and 1946996 (2). Density functional theory (DFT) was used to optimize the geometric structures for the S<sub>0</sub> and T<sub>1</sub> states of the ligands. In the framework of time-dependent density functional theory (TD-DFT), the geometry optimization for the  $S_1$  state was performed. The functional B3LYP combined with the basis set 6-311G\* was adopted. All of the DFT and TD-DFT calculations were carried out with the Gaussian 09 program package.<sup>27</sup> The UV-vis spectra were calculated by the TD-DFT method with the B3LYP/6-311G\* basis set.<sup>28</sup>

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Details of all the syntheses, characterizations, and measurements of the physical properties are presented in the Supporting Information.

#### RESULTS AND DISCUSSION

Syntheses and X-ray Crystal Structure Characterization. The ligands  $L_1$  and  $L_2$  were synthesized by the Sonogashira coupling reaction<sup>29</sup> of 4-ethynyl-*N*,*N*-bis(4methoxyphenyl)aniline and Br-bpy or I-xy-bpy (see the Supporting Information for details). The lanthanide complexes  $[Eu(tta)_3L_1]$  (1),  $[Sm(tta)_3L_1]$  (2), and  $[Eu(tta)_3L_2]$  (3) were synthesized by the reaction of the corresponding  $[Ln(tta)_3$ .  $2H_2O]$  precursors<sup>25</sup> with the ligand  $L_1$  or  $L_2$  in CH<sub>2</sub>Cl<sub>2</sub>/  $C_2H_5OH$  mixtures overnight. The Eu complex 3 was synthesized to explore whether the addition of a *p*-xylene spacer would affect the photophysical properties. The ligands and complexes were all characterized by <sup>1</sup>H NMR, elemental analysis, ESI-MS, and infrared (IR) spectroscopy. Single crystals of the ligand  $L_1$  and complexes 1 and 2 suitable for X-ray diffraction were obtained by diffusion of ethanol into the CH<sub>2</sub>Cl<sub>2</sub> solutions of the corresponding compounds. Their selected crystal data and data collection parameters are given in Table S1 in the Supporting Information.

Figure 1 shows the structure of  $L_1$ . It crystallizes in the monoclinic space group  $P2_1/c$  with two molecules per asymmetric unit. In these two independent molecules, the dihedral angles between the acetylene-bonded benzene ring and the bipyridine plane are different. The benzene ring (C45-C50) is almost coplanar with the corresponding acetylene-bonded bipyridine, twisting by 3.2°, and the acetylene group lies in the mean plane of the bipyridine. In the second molecule in this asymmetric unit, the benzene ring (C13-C18) is twisted out of planarity from the bipyridine (C1-C10) by approximately  $13.3^{\circ}$ . The dihedral angle between the plane of C16-C19-C26 and the plane of the bipyridine (C1-C10) is  $12.5^{\circ}$ , and it is  $6.5^{\circ}$  for the angle between the plane of C48-C51-C58 and the plane of the bipyridine (C33-C42). The nitrogen atoms and the connected carbon atoms in the triphenylamine group are coplanar; the dihedral angles between this plane and the adjacent benzene rings are 3.8, 84.9, 89.8, 13.1, 65.8, and 59.8°, respectively. The C $\equiv$ C bond lengths are 1.200 and 1.197 Å, and the C-C≡C angles are 174.9, 176.2, 176.5, and 178.4° (Table S2), which indicate that the  $-C \equiv C -$  chains slightly deviate from linearity. As shown in Figure 1b, the  $L_1$  molecules pack together by  $\pi \cdots \pi$  interactions between adjacent bipyridine-C $\equiv$ C-C<sub>6</sub>H<sub>4</sub> moieties and CH··· $\pi$  weak interactions to form a 3D network.

The single-crystal X-ray diffraction studies revealed that complexes 1 and 2 are isostructural. They both crystallize in the monoclinic space group  $P2_1/c$ , and their selected bond lengths and angles are given in Table S2. Here, complex 1 is taken as an example to describe their structures in detail. The asymmetric unit of 1 contains one ligand  $L_1$ , one  $Eu^{3+}$  ion, and three tta ligands. As depicted in Figure 2a, the  $Eu^{3+}$  ion is 8-fold coordinated by two N atoms from the bipyridine moieties in  $L_1$  and six O atoms from three bidentate  $\beta$ -diketonate tta ligands with Eu–N bond lengths of 2.598 and 2.627 Å, as well as Eu–O bond lengths of 2.350–2.396 Å. The coordination number of 8 is common for Eu<sup>3+</sup> complexes; the average Eu–O distance is 2.21 Å and that is 2.59 Å for average Eu–N distance.<sup>30</sup> Obviously, the Eu–O and Eu–N bond lengths of complex 1 are close to these average values. The coordination



**Figure 2.** (a) ORTEP drawing of  $Eu(tta)_3L_1$  (1). Hydrogen atoms are omitted for clarity, and thermal ellipsoids are shown at 50% probability. (b) Coordination polyhedron of the central  $Eu^{3+}$  (1) ion. Color code: blue for N, gray for C, red for O, purple-red for Eu.

polyhedron of the Eu<sup>3+</sup> center is illustrated in Figure 2b; the Eu atom finds itself in a distorted-trigonal-dodecahedral coordination geometry. The distance from Eu to the N atom in the triphenylamine group is about 11.624 Å. The C–C $\equiv$ C angles are 176.0 and 174.7°, deviating from linearity more strongly than in the free ligand  $L_1$ , and the C $\equiv$ C bond length is 1.198 Å. The plane of the benzene ring (C13–C18) deviates from the bipyridine plane by about 12.3°. In the triphenylamine moiety, the dihedral angles between the  $C \equiv C$  bond connected phenyl plane and the methoxyl group connected phenyl planes are 49.0 and 84.2°, and these benzene planes deviate from the C16-C19-C26 plane by about 26.4, 71.2, and 28.3°, respectively. The structure of complex 2 is shown in Figure S1. It has longer Ln-N and Ln-O distances and smaller N-Ln-N and O-Ln-O angles in comparison with complex 1, because Sm<sup>3+</sup> has a larger ionic radius of 1.079 Å in comparison with that of 1.066 Å for Eu<sup>3+</sup> (Table S2).<sup>31</sup>

**Optical Absorption and Emission Spectroscopy of the Ligands L**<sub>1</sub> **and L**<sub>2</sub>. The absorption and emission spectra of the free ligands L<sub>1</sub> and L<sub>2</sub> were measured in different solvents to study the solvatochromism phenomena. The absorption and emission spectra, absorption and emission  $\lambda_{max}$  values, molar absorption coefficients, and corresponding Stokes shift of L<sub>1</sub> are shown in Figures 3a and 4 and Table S3. In different solvents, the two maximum absorption peaks of L<sub>1</sub> are localized at ~290 and ~380 nm with a subtle solvent effect (Table S3). It has the largest and smallest molar absorption coefficients in CH<sub>2</sub>Cl<sub>2</sub> (9.16 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>) and ethanol (0.78 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>) for the ~380 nm absorption band, respectively. The first band at ~290 nm is assigned to the bpylocalized  $\pi \rightarrow \pi^*$  transition,<sup>32</sup> and the second band at ~380 nm is an intramolecular charge transfer band. DFT calculations



Figure 3. Absorption spectra of  $L_1$  (a) and  $L_2$  (b) in different solvents.



Figure 4. Emission spectra of  $L_1$  in different solvents at room temperature ( $\lambda_{ex} \approx 380$  nm).

with the Gaussian 09 program (Figure 5) demonstrate that this intramolecular charge transfer (CT) transition is from the HOMO mainly localized on the TPA group to the LUMO mainly localized on the bpy group. Both the HOMO and the LUMO have significant contributions to the C $\equiv$ C alkynyl linker, indicating that there is strong electronic coupling between the **TPA** and the bipyridine ligand. This will be important for the energy transfer studies reported below. TD-DFT calculations for the single-crystal structure of L<sub>1</sub> without optimization was carried out by the G09 program, using the B3LYP function with the basis set 6-311G<sup>\*</sup>, which was able to compute absorption spectra that were similar to the spectra with two experimentally observed absorption bands centered at 282 and 378 nm (Figure S2). For ligand L<sub>2</sub>, the intramolecular



**Figure 5.** Frontier orbitals with their charge density representations of  $L_1$  and  $L_2$  as calculated by DFT (B3LYP/6-311G\*).

charge transfer band from the HOMO to the LUMO moves to ~360 nm (Figure 3b and Table S4) in comparison to  $L_1$ , with the largest and smallest molar absorption coefficients in THF (4.22 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>) and ethanol (1.32 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>). Presumably, the torsion angle between the *p*-xylene and bipyridine moieties changes the full  $\pi$ -conjugation of the molecule, increasing the energy of the intramolecular charge transfer transition. Furthermore, the larger HOMO–LUMO energy gap for  $L_2$  in comparison with  $L_1$  is verified by the DFT calculations (Table S5).

The emission spectra of the ligands are strongly dependent on the selected solvents (Figure 4 and Figure S3 and Tables S3 and S4). A significant red shift in the emission of  $L_1$  was observed, with the luminescence band maximum changing from 473 nm in toluene to 547 nm in chloroform and 585 nm in ethanol (Figure 4). Very weak emission bands at  $\sim$ 440 and ~600-650 nm were found in methanol, acetone, dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), and acetonitrile (Figure S3). The emission of  $L_2$  also shows a pronounced red shift from 445 nm in toluene to 544 nm in dichloromethane and to 620 nm in acetonitrile (Figure S3). From Tables S3 and S4 we can see that, in the same solvent, the emission bands of L<sub>2</sub> are blue-shifted in comparison to the corresponding emission bands of  $L_1$ . We tentatively attribute this to the xylene group, which increases the excited energy level of L<sub>2</sub>.

**Optical Absorption Spectroscopy of Complexes 1–3.** The electronic spectra of complexes 1–3 were recorded in different solvents with a concentration of  $2 \times 10^{-5}$  M at room temperature (Figure 6 and Figure S4). The absorption maximum values and corresponding molar absorption coefficients are collected in Table S6. In most solvents, complex 1 shows two intense absorption bands at ~290 and ~340 nm, which are assigned to the  $\pi \to \pi^*$  transitions of the bpy and tta moieties.<sup>33</sup> Furthermore, in most solvents there is a shoulder near 390 nm, whereas in dichloromethane and toluene that shoulder becomes observable as a separate band



Figure 6. Absorption spectra of complexes 1 and 3 in different solvents.

with a peak at ~410 nm. We speculate that the shoulder at  $\sim$ 390 nm and the absorption band at  $\sim$ 410 nm are due to intramolecular charge transfer absorption, similar to what was observed above for the free ligands. In toluene and dichloromethane, the absorption band belonging to the  $\pi \rightarrow$  $\pi^*$  transition of the tta group are slightly blue shifted to ~330 nm, and this increases the spectral separation of  $\pi \to \pi^*$  and charge transfer absorption bands in these two particular solvents. The Sm complex 2 has similar absorption spectra in different solvents with absorption maxima at ~340 nm and also an absorption band at around 410 nm in both dichloromethane and toluene. The Eu complex 3 only shows two obvious absorption maxima at ~290 and ~340 nm in different solvents with a very small shift. No obvious absorption band around ~410 nm or tiny shoulder around 390 nm is found in the spectra, likely due to the xylene group introduced into the ligand, which changes its conjugation. Although we did not obtain the single-crystal structure of complex 3, we may try to study the difference in the structures of 1 and 3 by the DFT calculation results. In the optimized geometries of complexes 1 and 3, the dihedral angle between the bpy plane and the ethynyl connected benzene unit is only 7.56° for complex 1 but 49.58° for the complex 3. The dihedral angle between the p-xylene unit and the bpy plane is about 45.56°, and the pxylene and the ethynyl-connected benzene are almost coplanar with a dihedral angle of 3.98° in complex 3. From these data we may see that the addition of *p*-xylene unit changes the conjugation of the ligands, and there is a nearly 50° torsion

angle between the bpy group and the ethynyl-connected benzene group of **TPA** in complex **3** (the Cartesian coordinates of all the optimized geometries are shown at the end of the Supporting Information). Consequently, the intramolecular charge transfer of complex **3** is weakened. DFT calculations for the absorption spectra of complexes **1** and **3** with their optimized structures also confirm that **1** has one pronounced intramolecular charge transfer band, but for **3**, this band is not observable (Figure S5).

Solid-State and Solution PL Properties of Complexes 1-3. The steady-state room temperature photoluminescence (PL) of complexes 1-3 was measured in different solvents and in the solid state by exciting them at ~340 nm according to their absorption maximum values, respectively, and their spectra are shown in Figure 7 and Figure S6. The observed spectral data, lifetimes, and quantum yields of the complexes are collected in Table 1 and in Tables S6 and S7. The emission spectra of the Eu complexes 1 and 3 in the solid state (Figure S6) exhibit typical 4f-4f transitions of  ${}^{5}D_{0} \rightarrow {}^{7}F_{I}$  (J = 0-4) at 580, 591, 612, 652, and 702 nm. The addition of the p-xylene group also increases the asymmetric ligand fields around Eu ions in complex 3, resulting in the emission intensity of  ${}^{5}D_{0} \rightarrow$  ${}^{7}F_{0}$  and  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transitions changing in comparison with complex 1, especially for the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  hypersensitive transition (Figure S6). The emission of Sm complex 2 in the solid state yields relatively broad bands, observed at about 562, 597, 644, and 705 nm, which are assigned to the  ${}^{4}G_{5/2} \rightarrow {}^{6}H_{I}$ (J = 5/2, 7/2, 9/2, 11/2) transitions, and very tiny signals at 875 ( ${}^{4}G_{5/2} \rightarrow {}^{6}F_{1/2}$ ) and 945 ( ${}^{4}G_{5/2} \rightarrow {}^{6}F_{5/2}$ ) nm were detected belonging to the NIR emission of Sm<sup>3+</sup> (Figure S6). The time-resolved emission decay measurements reveal biexponential decays with lifetimes of 0.7 and 2.9  $\mu$ s for 1, 1.2 and 7.0  $\mu$ s for 2, and 39.4 and 220  $\mu$ s for 3, respectively. There are two hypotheses in the literature to explain this biexponential decay: (i) a back transfer from the metal to the triplet state of the organic ligand and (ii) the radiative decay of two different excited species.<sup>34a</sup> Fujiwara et al. observed a biexponential decay of two Eu complexes with 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione and 4,7-diphenyl-1,10-phenanthroline disulfonate ligands at the toluene-water interface,<sup>34</sup> and one is  $Eu(tta)_2bps^-$  (long lifetime) and another is  $Eu_2(tta)_2(bps)_2$  (short lifetime). That seems not possible in our case because the lifetimes of our complexes were obtained in the solid state. Therefore, the possible reason for these biexponential decays is the back transfer from the metal to the triplet state of the organic ligand. Complexes 1 and 3 luminesce with quantum yields of 0.3% for 1 and 8.7% for 3 in the solid state at room temperature following excitation at 340 nm. The underlying reason for the lower quantum yield of 1 is probably that ligand  $L_1$  has lower energy levels, in favor of energy transfer from Eu<sup>3+</sup> ions to the ligands.

In solution, the steady-state emission spectra of the three complexes exhibit strong solvent effects; their absorption and emission data are summarized in Table S6. Complexes 1 and 3 show the typical emission of Eu<sup>3+</sup> ions, with emission bands at around 580, 591, 612, 652, and 702 nm, which are assigned to  ${}^{5}\text{D}_{0} \rightarrow {}^{7}\text{F}_{J}$  (J = 0-4) transitions of Eu<sup>3+</sup> in more polar solvents such as DMSO, DMF, acetone, C<sub>2</sub>H<sub>5</sub>OH, CH<sub>3</sub>OH, and CH<sub>3</sub>CN. However, additional emission bands attributable to the free ligands L<sub>1</sub> and L<sub>2</sub> are present in less polar solvents, e.g., CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>Cl, THF, toluene, and ethyl acetate (EAC) (Figure 7). Complex 1 shows the emission of the ligand L<sub>1</sub> at about 470 nm (toluene), ~535 nm (CHCl<sub>3</sub>, EAC, and THF),



Figure 7. Emission spectra of complexes 1 (a), 2 (c), and 3 (e) in different solvents ( $2 \times 10^{-5}$  M) with ~340 nm excitation and the white-light emission CIE color gamuts of complexes 1 (b) cross 1 (EAC,  $\lambda_{ex} = 343$  nm) and cross 2 (THF,  $\lambda_{ex} = 348$  nm), 2 (d) cross 1 (DCM,  $\lambda_{ex} = 334$  nm), cross 2 (DCM,  $\lambda_{ex} = 426$  nm), and cross 3 (toluene,  $\lambda_{ex} = 355$  nm), and 3 (f) cross 1 (CHCl<sub>3</sub>,  $\lambda_{ex} = 343$ ), cross 2 (EAC,  $\lambda_{ex} = 344$  nm), and cross 3 (THF,  $\lambda_{ex} = 348$  nm).

## Table 1. Photophysical Properties of Complexes 1–3 in CH<sub>3</sub>CN Solution at Room Temperature

complex	$\Phi^a$ (%)	$ au_{\mathrm{obs}}^{b}(\mu \mathrm{s})$	$k_{\rm r}^{\ c}~({\rm s}^{-1})$	$k_{\rm nr}^{\ d} \ (10^3 \ {\rm s}^{-1})$
1	2.6	646	40.2	1.51
2		104		
3	1.8	646	27.9	1.52

"Emission quantum yields of the complexes following excitation at 340 nm in CH<sub>3</sub>CN. <sup>b</sup>Excited-state lifetimes of the complexes following excitation at 340 nm in CH<sub>3</sub>CN <sup>c</sup>k<sub>r</sub> =  $\Phi/\tau_{\rm obs}$ . <sup>d</sup>k<sub>nr</sub> =  $1/\tau_{\rm obs} - k_r^{.35}$ 

and 554 nm (DCM). For complex 3, the emission bands belonging to the ligand  $L_2$  are blue-shifted by about 25–45 nm in comparison with complex 1, because the introduction of the *p*-xylene spacer in the ligand  $L_2$  increases the energy levels of the excited states of the ligand, which is also verified by DFT calculations (Table S5), as noted above.

The Sm complex may in principle show emission not only in the visible but also in the NIR region. Indeed, weak emission at 883 and 950 nm is observed on excitation of complex **2** at 340 nm in CH<sub>3</sub>CN (Figure S7), due to the  ${}^{4}G_{5/2} \rightarrow {}^{6}F_{1/2}$  and  ${}^{4}G_{5/2}$  $\rightarrow {}^{6}F_{5/2}$  transitions of Sm<sup>3+</sup>. Here, we will focus on the emission in the visible region of complex **2**. Clearly, complex **2** 

exhibits different photoluminescence properties in comparison with complexes 1 and 3. In more polar solvents such as acetonitrile and acetone, the emission of Sm<sup>3+</sup> ions exhibits peaks at about 560, 598, 645, and 705 nm in the visible region, which are assigned to the 4f–4f transitions  ${}^{4}G_{5/2} \rightarrow {}^{6}H_{5/2}$ ,  ${}^{4}G_{5/2} \rightarrow {}^{6}H_{7/2}$ ,  ${}^{4}G_{5/2} \rightarrow {}^{6}H_{9/2}$ , and  ${}^{4}G_{5/2} \rightarrow {}^{6}H_{11/2}$ , respectively. However, unlike complexes 1 and 3, in methanol, ethanol, DMF, and DMSO, complex 2 shows not only the intense emission of Sm<sup>3+</sup> ions but also a weak emission of the L<sub>1</sub> ligand at about 430 nm. In less polar solvents such as dichloromethane, chloroform, THF, and ethyl acetate (EAC), it exhibits strong and broad emission of the ligands and weak emission of Sm<sup>3+</sup> ions. In toluene, 2 only shows a strong emission band from the ligand, which is different from the case for the Eu complexes. These different solvent-dependent luminescent behaviors of complexes 1 and 3 on the one hand and complex 2 on the other hand are due to the different excited energy levels of  $Eu^{3+}$  (<sup>5</sup>D<sub>0</sub>) and  $Sm^{3+}$  (<sup>4</sup>G<sub>5/2</sub>).

The time-resolved emission of complexes 1-3 was studied by monitoring the samples at 612 nm  $({}^{5}D_{0} \rightarrow {}^{7}F_{2})$  for the Eu complexes and at 645 nm ( ${}^{4}G_{5/2} \rightarrow {}^{6}H_{9/2}$ ) for the Sm complex in different solvents (Figure S8). In all investigated solvents, single-exponential decays with lifetime on the microsecond time scale were obtained (Table S7). Complex 1 has the largest  $au_{\rm obs}$  value of 712  $\mu s$  in DMSO and the smallest  $au_{\rm obs}$ value of 232  $\mu$ s in MeOH. Complexes 2 and 3 have their largest  $\tau_{obs}$  values in CH<sub>3</sub>CN of 104  $\mu$ s for 2 and 646  $\mu$ s for 3, and the smallest  $au_{obs}$  values of 16  $\mu s$  for 2 and 279  $\mu s$  for 3 occur in MeOH. In CH<sub>3</sub>CN solution, all of these complexes exhibit pure emission of  $Ln^{3+}$  (and no ligand emission); therefore, we take their quantum yields and the lifetime values obtained in CH<sub>3</sub>CN to determine the radiative  $(k_r)$  and nonradiative  $(k_{nr})$  excited-state decay rate constants of these complexes, and all of the selected data are summarized in Table 1.

The luminescence quantum yields for the Eu complexes 1 and 3 are 2.6% and 1.8%, and the corresponding  $k_r$  values for 1 and 3 are 40.2 and 27.9 s<sup>-1</sup> in CH<sub>3</sub>CN solution, respectively. From Table 1, we can see that complex 1 shows close  $k_r$  and  $k_{nr}$  values in comparison with complex 3 in CH<sub>3</sub>CN. The emission of Sm complex 2 is too weak to allow evaluation of its quantum yield both in the solid state and in CH<sub>3</sub>CN solution.

White-Light Emission. Single-component white-light emitters have attracted increasing attention, as they will in principle simplify the preparation of optical display devices by avoiding the mixing of two (blue/yellow) or three (red/blue/green) separate components. According to the 1931 CIE (International Commission on Illumination) coordinate diagram, standard white light should have the CIE coordinates (0.33, 0.33). Recently, some lanthanide complexes were reported as white-light emitters.<sup>36</sup> The white-light emission of complex 2 in EAC solution under a 365 nm UV lamp excitation (Figure S9) inspired us to study the application potential of complexes 1–3 as white-light-emitting materials.

The room-temperature emission spectra of complexes 1-3 in different solvents and the corresponding chromaticity diagrams in selected solvents are shown in Figure 7, which reveals that the CIE coordinates of these complexes (summarized in Tables S8– S10) may indeed be located favorably in the white-light region. The CIE coordinates of complex 1 are (0.31, 0.33) (cross 1 in Figure 7b) in ethyl acetate (EAC) on excitation at 343 nm and (0.31, 0.31) (cross 2 in Figure 7b) in THF on excitation at 348 nm. When

complex 2 is excited at 334 and 426 nm in DCM or at 355 nm in toluene, it may generate white-light emission with CIE coordinates of (0.34, 0.30) (cross 1 in Figure 7d), (0.34, 0.33) (cross 2 in Figure 7d), and (0.33, 0.35) (cross 3 in Figure 7d), respectively. The Eu complex 3 generates white-light emission when it is excited at 343 nm in CHCl<sub>3</sub> (0.31, 0.31) (cross 1 in Figure 7f), at 344 nm in EAC (0.33, 0.32) (cross 3 in Figure 7f), and at 348 nm in THF (0.33, 0.32) (cross 3 in Figure 7f). It is obvious from Figure 7a,c,e that the corresponding complexes in the respective solvents exhibit emission both from the ligands and from the  $Ln^{3+}$  ions, and the proper mixtures of emissions from  $Ln^{3+}$  ions and the ligands produce the white light.

Electrochemistry and UV/Vis/NIR Spectroelectrochemistry Studies. The electrochemical properties of the lanthanide complexes 1-3 were explored by cyclic voltammetry (CV) in acetonitrile solution with  $(n-C_4H_9)_4NPF_6$  as the electrolyte (0.1 mol dm<sup>-3</sup>). Cyclic voltammograms are shown in Figure S10 in the Supporting Information. Complexes 1-3display one reversible one-electron oxidation with half-wave potentials of 0.36, 0.38, and 0.30 V (vs. Fc<sup>+</sup>/Fc), respectively. These oxidation waves are attributed to the TPA<sup>•+</sup>/TPA redox couples in the ligands  $L_1$  and  $L_2$ , whose radical cations are stable on the voltammetric time scale due to the high degree of chemical reversibility. The Eu complexes 1 and 3 show irreversible reductions of the metal center at about -2.15 and -2.20 V, respectively. The Sm complex 2 does not show any redox signal for the metal center. Actually, it has been reported in the literature that the  $E_{\rm pc}$  value of Eu<sup>3+/2+</sup> is -1.78 V (vs  $Fc^+/Fc)$  for the complex  $[Eu(BPPA)_2]OTf$  and -1.77 V (vs  $Fc^+/Fc)$  for  $[Eu(BPA)_2]OTf$ , and the value is even more negative and not observable for the complex  $[Eu(MPA)_2K]$ under the same conditions.<sup>37</sup> Normally, the  $E_{1/2}(Sm^{3+/2+})$ value should be more negative than  $E_{1/2}(\text{Eu}^{3+/2+})$  as reported in the literatures.<sup>37,38</sup> That is the reason that complex 2 does not present any redox event. Such negative reduction potential for these complexes make the photoinduced electron transfer from the TPA group to the excited Ln<sup>3+</sup> ions impossible according to the Rehm-Weller equation.<sup>39</sup>

Triphenylamine derivatives have good electrochromic properties; normally their UV-vis absorption spectra change upon oxidation.<sup>22</sup> To investigate the absorption spectra variation with applied electrochemical potential, the accessible redox states of complex 1 were produced in a thin-layer cuvette with an Ag wire as the reference electrode, a Pt rod as the counter electrode, and a Pt net as the working electrode. A deaerated CH<sub>3</sub>CN solution with 0.25 mol dm<sup>-3</sup> (n- $C_4H_9)_4NPF_6$  as the supporting electrolyte was used. At an applied potential of 1.2 V vs Ag<sup>+</sup>/Ag, the spectroelectrochemistry was studied. Figure 8 shows the spectral changes of complex 1. Upon oxidation, the absorption band at about 340 nm decreases, and a new absorption band at 760 nm appears, which is assigned to the absorption of the radical cation TPA<sup>•+</sup>. This is also confirmed by measuring the absorption spectra of the oxidized 1<sup>•+</sup> generated by addition of 1 equiv of ceric ammonium nitrate (CAN) oxidant (Figure S11).

Luminescence Control and Tuning by Applying an Electrochemical Potential. To explore luminescence switching upon application of an external potential for complexes 1 and 2, their emission spectra were measured as a function of electrochemical potential. Using the same experimental setup as in the UV/vis/NIR spectroelectrochemistry study, the emission spectra were detected in a thin-layer cuvette.



Figure 8. UV/vis/NIR spectroelectrochemistry in  $CH_3CN/(n-C_4H_9)_4NPF_6$ : oxidation of 1 to 1<sup>•+</sup> at a potential of 1.2 V vs Ag<sup>+</sup>/Ag. The asterisk marks an instrumental artifact caused by a lamp changeover in our spectrometer.

Complexes 1 and 2 show pure emission of  $Eu^{3+}$  and  $Sm^{3+}$  ions in CH<sub>3</sub>CN in their neutral forms (see the black curves in Figure 9a,b), but no ligand emission. When 1.2 V potential (vs  $Ag^{+}/Ag$ ) was applied in the solution inside the cuvettes, the emission signals were strongly quenched (the red curves in Figure 9a,b), and when the potential was changed to -0.3 V (vs Ag<sup>+</sup>/Ag), the emission was almost completely recovered (the blue curves in Figure 9a,b). To test the reversibility of luminescence switching of complexes 1 and 2, six cycles of  $1 \rightarrow$  $1^{\bullet+} \rightarrow 1$  and  $2 \rightarrow 2^{\bullet+} \rightarrow 2$  emission measurements were performed in our setup, and the luminescence switching spectra were detected. The emission intensities at 612 nm for 1 and 645 nm for 2 were considered to make graphs of the on/ off switching experiments (Figure 9c-f). After six cycles, the emission intensity decreased to 86% of the initial intensity for 1 and 82% for 2. From their emission spectra of the last recovery, no additional emission signals were detected and the emission intensity decrease perhaps came from small amounts of oxygen involved in the solution during the measurements. The underlying reason for the luminescence switching is energy transfer from the  $Eu^{3+}$  or  $Sm^{3+}$  ions to the  $L_1^{\bullet+}$  radical cation, which will be discussed in the following section.

Influence of the Chemical Oxidant CAN on Luminescence. In principle, chemical oxidants should also be able to oxide the complexes and produce the TPA<sup>++</sup> radical cations with the positive charge localized,<sup>22,32</sup> which may then induce



**Figure 9.** Luminescence switching study of complexes 1 and 2 by investigation of the emission signal at 612 nm of 1 (a, c, e) and at 645 nm of 2 (b, d, f) in deaerated acetonitrile with 0.25 M (n- $C_4H_9$ )<sub>4</sub>NPF<sub>6</sub> by alternating the applied electrochemical potential between 1.2 V and -0.3 V (vs Ag<sup>+</sup>/Ag).

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Figure 10. Emission spectra and luminescence decay curves for complexes 1 (a, b), 2 (c, d) and 3 (e, f) with and without 1 equiv CAN in CH<sub>3</sub>CN solution ( $\lambda_{ex} = 340 \text{ nm}$ ,  $\lambda_{em} = 612 \text{ nm}$  for 1 and 3,  $\lambda_{em} = 645 \text{ nm}$  for 2).

the intramolecular energy transfer from  $Eu^{3+}$  or  $Sm^{3+}$  ions to **TPA**<sup>++</sup>, resulting in luminescence quenching similar to that observed above. To explore this aspect, 1 equiv of ceric ammonium nitrate (CAN) was used to oxidize complexes 1-3 in acetonitrile. Upon excitation of the complexes at 340 nm, their corresponding steady-state emission spectra and time-resolved photoluminescence decay with and without CAN were studied. Figure 10 shows that the 612 nm emissions of Eu complexes 1 and 3 are almost completely quenched, but for the Sm complex 2, the emission at 645 nm is only partially quenched.

We also compared the time-resolved luminescence decays of complexes 1-3 in their neutral and oxidized forms in CH<sub>3</sub>CN solution. Three identical single-exponential decays were observed, and the lifetimes of the excited states were determined as 646  $\mu$ s (1 and 3) and 104  $\mu$ s (2) (Table 1). When they were oxidized by 1 equiv of CAN, the excited-state lifetimes of the one-electron-oxidized forms were  $102 (1^{\bullet+}), 66$  $(2^{\bullet+})$  and 117  $(3^{\bullet+}) \mu s$ , respectively. We take Eu $(tta)_3$  bpy and Sm(tta)<sub>3</sub>bpy as the reference complexes, whose excited-state lifetimes are 630 and 85  $\mu$ s (Figure S12). The energy transfer rate constants  $k_{\rm ET}$  for Ln(III)\*  $\rightarrow$  TPA<sup>•+</sup> (the positive charge localized on the TPA moiety of ligands) in complexes  $1^{\bullet+}$ ,  $2^{\bullet+}$ and  $3^{\bullet+}$  can be calculated as  $8.2 \times 10^3$ ,  $3 \times 10^3$  and  $6.9 \times 10^3$ s<sup>-1</sup> according to eq 1,<sup>40</sup> where  $\tau_{\rm complex}$  is the excited-state lifetime of complexes 1<sup>•+</sup>, 2<sup>•+</sup>, and 3<sup>•+</sup> and  $\tau_{\rm ref}$  is the lifetime of the excited state of reference complex Eu(tta)<sub>3</sub>bpy or  $Sm(tta)_3bpy.$ 

$$k_{\rm ET} = \tau_{\rm complex}^{-1} - \tau_{\rm ref}^{-1} \tag{1}$$

Intramolecular Energy Transfer in the Neutral and Oxidized Forms of Complexes 1 and 2. The above observations strongly point to intramolecular energy transfer, and it is desirable to understand these energy transfer processes between the ligands and the Ln<sup>3+</sup> ions in greater detail. According to the energy transfer mechanism in lanthanide complexes proposed by Crosby et al.,<sup>41</sup> the energy level match between the  $Ln^{3+}$  ions ( ${}^{5}D_{0}$  for  $Eu^{3+}$  in 1,  ${}^{4}G_{5/2}$  for  $Sm^{3+}$  in 2) and the triplet states of the free ligands (tta and  $L_1$ ) strongly affects the luminescence properties of the lanthanide complexes. There are two ligands, L1 and tta, in complexes 1 and 2. To clarify the intramolecular energy transfer processes in our complexes, the relevant singlet and triplet energy levels of L1 and tta ligands should be identified. As reported in the literature,<sup>42</sup> the tta ligand has an excited singlet energy of 3.12 eV (25164 cm<sup>-1</sup>) and its triplet energy is 2.35 eV (18954  $cm^{-1}$ ). The UV-vis absorption edge of  $L_1$  in CH<sub>3</sub>CN at room temperature is estimated as its singlet energy level. The lower wavelength emission peaks of the phosphorescence spectra of the gadolinium complex at 77 K is used to calculate the triplet energy level of L1, because the lowest excited energy level of  $Gd^{3+}$  ions (<sup>6</sup>P<sub>7/2</sub>) is very high (3.99 eV, 32150 cm<sup>-1</sup>),<sup>43</sup> and therefore energy transfer cannot interfere. The absorption edge of  $L_1$  (Figure 3a) is 460 nm, corresponding to 21739 cm<sup>-1</sup> (2.70 eV). The lower wavelength emission peak of the  $GdL_1$ complex at 77 K is 506 nm (2.45 eV, 19762 cm<sup>-1</sup>) (Figure S13). The energy levels of the relevant excited states for the ligands  $L_1$  and tta are summarized in Table 2.

## Table 2. Relevant Excited-State Energies of $L_1$ , $L_1^{\bullet+}$ , tta, $Eu^{3+}$ , and $Sm^{3+}$

entry	singlet energy level $(eV/cm^{-1})$	triplet energy level (eV/cm <sup>-1</sup> )
tta	3.12/25164	2.35/18954
$L_1$	2.70/21739	2.45/19762
$L_1^{\bullet+}$	1.65/13333	<1.65/<13333 <sup>a</sup>
Eu <sup>3+</sup>		$2.02/17500 ({}^{5}D_{0} - {}^{7}F_{2})^{b}$
Sm <sup>3+</sup>		$1.91/17900({}^{4}G_{5/2} - {}^{6}H_{9/2})^{b}$

<sup>*a*</sup>In this case, it is the lowest excited energy level of  $L_1^{\bullet+}$ , not the triplet energy level. <sup>*b*</sup>Energy estimate taken from the most intense emission line of  $Ln^{3+}$ .

As a rule of thumb, the energy difference between the triplet excited state of ligands and the emitting energy level of Ln<sup>3+</sup> should be between 2500 and 4000 cm<sup>-1</sup> for efficient energy transfer.<sup>44,45</sup> The emissive <sup>5</sup>D<sub>0</sub> excited state of Eu<sup>3+</sup> is at an energy of 17500 cm<sup>-1,46</sup> The energy level difference between  $T_1$  of  $L_1$  and  ${}^5D_0$  of Eu<sup>3+</sup> is only 2262 cm<sup>-1</sup>, which suggests that the energy transfer of  $T_1 \rightarrow {}^5D_0$  is not very efficient, resulting in the possibility of backward energy transfer from the metal to the ligand. Moreover, the energy level difference between the singlet and triplet excited states of L1 is only 1977  $cm^{-1}$ , significantly less than 5000  $cm^{-1}$ , which may in principle lead to the back intersystem crossing from the  $T_1$  to  $S_1$  excited state of L<sub>1</sub>. The intersystem crossing of  $S_1 \rightarrow T_1$  can be very effective only when the energy gap  ${}^{1}\pi\pi^{*}-{}^{3}\pi\pi^{*}$  is greater than 5000 cm<sup>-1</sup> according to Reinhoudt's empirical rule.<sup>47</sup> An energy level diagram and possible energy transfer processes are summarized in Figure 11. Different plausible reaction sequences are as follows. (i) The tta ligands absorb excitation light, and intersystem crossing from the  $S_1$  to  $T_1$  excited state of tta occurs. Subsequently, energy transfer to the  ${}^{5}D_{0}$  excited state of Eu<sup>3+</sup> to sensitize the characteristic red emission of Eu<sup>3+</sup> occurs. (ii) The L<sub>1</sub> ligand harvests energy and intersystem conversion from its  $S_1$  to its  $T_1$  level takes place; however, the reverse intersystem crossing may occur due to the small energy gap  ${}^{1}\pi\pi^{*}-{}^{3}\pi\pi^{*}$  (1977 cm<sup>-1</sup>), leading to the ligand-centered fluorescence from  $S_1$ , as well as some energy transfer from  $T_1$ of  $L_1$  to  ${}^5D_0$  of  $Eu^{3+}$ .

The energy levels of  $L_1$  are of key importance for the intramolecular energy transfer in complexes 1 and 2. On the basis of the emission spectra (Figure 4 and Figure S3), it is clear that the energies of the relevant excited states of the ligands vary in different solvents according to the emission spectra. When the  $\Delta E(\pi\pi\pi^*-\pi\pi\pi^*)$  value of the ligand is high enough to prevent the reverse intersystem crossing, complex 1 exhibits pure red emission of Eu<sup>3+</sup>. Otherwise, the emission spectra exhibit mixed ligand-centered emission and Eu<sup>3+</sup> ion emission, leading to spectacular white-light luminescence. For Sm complex 2, the  ${}^{4}G_{5/2}$  energy level of Sm<sup>3+</sup> is located at 17900 cm<sup>-1</sup>,  ${}^{47}$  400 cm<sup>-1</sup> higher than the  ${}^{5}D_{0}$  state of Eu<sup>3+</sup>, and the energy difference between  $T_1$  of  $L_1$  and  ${}^4G_{5/2}$  of Sm<sup>3+</sup> is only 1862 cm<sup>-1</sup>, leading to more efficient backward energy transfer from  ${}^{4}G_{5/2}$  of Sm<sup>3+</sup> to the T<sub>1</sub> state of L<sub>1</sub> and further intersystem crossing to the  $S_1$  state of  $L_1$ , which results in more  $S_1$  emission from  $L_1$  in some less polar solvents (Figure 7 and Figure S14). Furthermore, according to our DFT calculations, the  $S_1$  and  $T_1$  energies of  $L_1$  are 2.32 eV (18726 cm<sup>-1</sup>) and 2.18 eV  $(17574 \text{ cm}^{-1})$ , respectively. Thus, the



Figure 11. Intersystem crossing (ISC) and energy transfer (ET) processes in 1 (a) and  $1^{\bullet +}$  (b).

 $\Delta E(\pi\pi\pi^*-\pi\pi\pi^*)$  value of L<sub>1</sub> is 1152 cm<sup>-1</sup>, and the energy differences between  $T_1$  of  $L_1$  and the emitting level of  $Ln^{3+}$  are 74 ( ${}^{5}D_{0}$  of Eu ${}^{3+}$ ) and -326 ( ${}^{4}G_{5/2}$  of Sm ${}^{3+}$ ) cm ${}^{-1}$ . Such small values do not favor energy transfer from  $L_1$  to  $Ln^{3+}$ , and backward energy transfer can lead to the emission of  $L_1$ , which is in agreement with the experimental results. However, considering the possible dissociation of ligands from the complexes in some solvents, the ligand-centered emission perhaps comes from the dissociated ligands. The dissociation of ligands from the complexes may change the ligand fields around Ln<sup>3+</sup>, which will lead to different excited species with different lifetimes. The single-exponential decays of the complexes in different solvents (Table S7 in the Supporting Information) indicate that the dissociation of ligands from the complexes is not enough to change the ligand fields of Ln<sup>3+</sup>, and it can be ignored due to the tiny amount. Therefore, we will not discuss the possibility that the dissociation of ligands from the complexes results in the ligand-centered emission here in detail.

As we know, **TPA**<sup>•+</sup> may be oxidized to a **TPA** radical dication, and one may suppose that the photoinduced electron transfer can happen in the oxidized complexes. **TPA**<sup>•+</sup> is reported to be oxidized to its radical dication at 0.8 V vs Fc<sup>+</sup>/ Fc.<sup>48</sup> On the basis of the reduction potential of Ln<sup>3+/2+</sup> and the excited energy of Ln<sup>3+</sup>, the  $\Delta G^{\circ}$  value for the photoinduced electron transfer in the oxidized complexes will be more than 0.63 eV for complex 1 and even more postitive for complex 2 according to the Rehm–Weller equation. It is obviously thermodynamically impossible for photoinduced electron transfer from **TPA**<sup>•+</sup> to the excited Ln<sup>3+</sup> to occur. When complex 1 or 2 was oxidized, a new band at 760 nm (1.65 eV,

13333 cm<sup>-1</sup>) belonging to the absorption of the nonemissive **TPA**<sup>•+</sup> appeared, and the corresponding excited energy levels of  $\mathbf{L_1}^{\bullet+}$  should be below 1.65 eV. The energy difference between the Ln<sup>3+</sup> and excited energy level of  $\mathbf{L_1}^{\bullet+}$  is therefore expected to be larger than 4167 cm<sup>-1</sup> for Eu (<sup>5</sup>D<sub>0</sub>), and larger than 4567 cm<sup>-1</sup> for Sm (<sup>4</sup>G<sub>5/2</sub>). These energy difference are suitable for the effective energy transfer from Ln<sup>3+</sup> to the radical cation of  $\mathbf{L_1}^{\bullet+}$ , resulting in luminescence quenching. The rate constant  $k_{\rm ET}$  of energy transfer for Ln<sup>3+\*</sup>  $\rightarrow$  **TPA**<sup>++</sup> for complex 1 (8.2 × 10<sup>3</sup> s<sup>-1</sup>) is greater than that for 2 (3 × 10<sup>3</sup> s<sup>-1</sup>), and so the luminescence is completely quenched for 1<sup>•+</sup> but only partially quenched for 2<sup>•+</sup>.

#### CONCLUSIONS

In summary, we have designed and synthesized the two new ligands L<sub>1</sub> (TPA-bpy) and L<sub>2</sub> (TPA-xy-bpy) with a triphenylamine unit as a redox center and bipyridine as a coordination ligand. The three corresponding lanthanide complexes Eu- $(tta)_{3}L_{1}$  (1), Sm $(tta)_{3}L_{1}$  (2), and Eu $(tta)_{3}L_{2}$  (3) have been also synthesized and characterized. The single-crystal structures of 1 and 2 reveal that  $Ln^{3+}$  is 8-fold coordinated in a distorted-trigonal-dodecahedral coordination geometry. Detailed photophysical investigations of  $L_1$ ,  $L_2$ , and complexes 1-3 demonstrate that the emission properties are strongly solvent dependent. In more polar solvents the complexes mainly show  $Ln^{3+}$  4f-4f emissions, whereas in less polar solvents they exhibit additional ligand-centered luminescence, leading to white-light emission in some solvents. Biexponential decays are determined in the solid states, but single-exponential decays are observed in the investigated solvents for all of the complexes. The lifetimes of the excited Eu<sup>3+</sup> (<sup>5</sup>D<sub>0</sub>) and Sm<sup>3+</sup>  $({}^{4}G_{5/2})$  states in these complexes are all on the microsecond scale both in the solid state and in solution. A UV/vis/NIR spectroelectrochemistry study indicates that the complexes show a new absorption band at 760 nm at an applied potential of 1.2 V vs  $Ag^+/Ag$ , which is assigned to the absorption of the radical cation TPA++. Complexes 1 and 2 show reversible luminescence switching properties upon application of an electrochemical potential, due to the intramolecular energy transfer from the Eu<sup>3+</sup> or Sm<sup>3+</sup> ions to the electrochemically generated TPA<sup>++</sup> radical cation. The intramolecular energy transfer in complexes 1 and 2 and their oxidized forms have been discussed on the basis of both the experimental results and the DFT calculations. Our work developed novel single molecular lanthanide complexes exhibiting white-light emission in some solvents and electrofluorochromic properties, which may have potential applications for lanthanide sensing, as well as for photoelectric and biomarker materials.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00392.

Additional synthetic and structural details, crystallographic data, theoretical calculations, and additional figures and tables as described in the text (PDF)

#### Accession Codes

CCDC 1946992 and 1946995–1946996 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/ cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

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