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## Self-assembly of Terbium(III)-based metal–organic complexes with two-photon absorbing active



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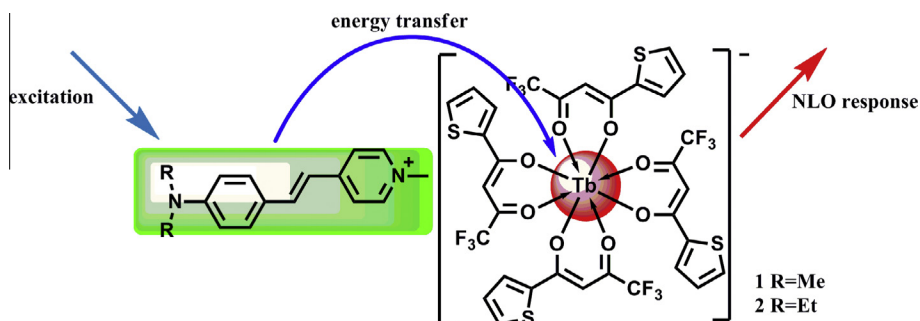
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## HIGHLIGHTS

- Hybrid Tb(III) complexes based on D- $\pi$ -A type dyes have been synthesized.
- The structural features of them were systematic studied.
- Linear absorption and emission spectra have been systematically investigated.
- The energy transfer takes place from the pyridinium (**2'**) cation to Tb(III).

## GRAPHICAL ABSTRACT

Hybrid complexes based on D- $\pi$ -A type dyes *p*-aminostyryl-pyridinium and Terbium(III) complex anion (**1**, **2**) have been synthesized by ionic exchange reaction. Meanwhile two different alkyl-substituted amino groups were used as electron donors in organic dyes cations. Their linear properties have been systematically investigated by absorption spectra and fluorescence, the results show that the energy transfer takes place from the trans-4-[4'-(N,N-diethylamino)styryl]-N-methyl pyridinium (**2'**) cation to Tb(III). In addition, complex **2** exhibit a large two-photon absorption coefficient  $\beta$ : 0.044 cm/GW at 710 nm.



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## ABSTRACT

Hybrid complexes based on D- $\pi$ -A type dyes *p*-aminostyryl-pyridinium and Terbium(III) complex anion (**1**, **2**) have been synthesized by ionic exchange reaction. Meanwhile two different alkyl-substituted amino groups were used as electron donors in organic dyes cations. The synthesized complexes were characterized by element analysis. In addition, the structural features of them were systematic studied by single crystal X-ray diffraction analysis. Their linear properties have been systematically investigated by absorption spectra and fluorescence, the results show that the energy transfer takes place from the trans-4-[4'-(N,N-diethylamino)styryl]-N-methyl pyridinium (**2'**) cation to Tb(III). In addition, complex **2** exhibit a large two-photon absorption coefficient  $\beta$ : 0.044 cm/GW at 710 nm.

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## Introduction

The design and synthesis of metal–organic complexes have attracted much attention due to their intrinsic physicochemical properties which promote applications in the areas of luminescent

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materials, heterogeneous catalysis, magnetism, and electrochemistry, as well as their intriguing variety of architectures and topologies [1–10]. In this area, one important branch is the construction of lanthanide-based metal–organic complexes because of their potential applications in fluoroimmunoassays [11], spectroscopic structural probes in biological systems [12], laser systems [13], optical amplification [13], organic light-emitting diodes [14], single-molecule magnets [15,16], and pressure/damage sensors [17] owing to their unique luminescence properties, such as the characteristic narrow-line emission and long luminescence lifetimes [18–26].

Along with the development of two-photon absorption (TPA) materials [27,28] and ultrafast lasers, two-photon scanning microscopy have been used extensively. Two-photon absorption materials extends the excitation wavelength to the long-wavelength region, which is in favor of less-harmful labeling and deep-penetrating bioimaging applications [29–32]. Therefore, with a combination of the advantages of both lanthanide and two-photon scanning microscopy, two-photon absorption lanthanide complexes attracts great attention [33–36], in which the TPA active is aroused via TPA of chromophores and subsequent energy transfer to the lanthanide ions. However, examples for the lanthanide complexes with excellent TPA properties are still very limited.

To achieve effective two-photon sensitized probes, the “antennae” with efficient two-photon absorption (TPA) for light-harvesting are needed to overcome the poor extinction coefficients of the Ln(III) ions caused by the symmetry-forbidden nature of the inner-shell  $f-f$  transition [38]. Initially, the “antenna” effects were utilized to sensitize the luminescence of Eu(III) and Tb(III), which were directly linked to proteins, nucleic acids, and biologically relevant chromophores [38,39]. Accordingly, in the present work, we report two novel Tb(III) complex (as shown in Scheme 1) that meets the urgent need described above. In these complexes, the important point is using trans-4-[p-(N,N-dialkylamino)styryl]-N-methylpyridinium as a one- and two-photon sensitizer for Tb(III) ion. The photophysical properties demonstrate that the energy transfer takes place from the trans-4-[4'-(N,N-diethylamino)styryl]-N-methyl pyridinium (**2'**) cation to Tb(III) and complex **2** exhibit a large two-photon absorption coefficient  $\beta$ : 0.044 cm/GW at 710 nm.

## Experiments

### General

All chemicals used were of analytical grade and the solvents were purified by conventional methods before use. The  $^1\text{H}$  NMR spectra were performed on Bruker 400 MHz spectrometer with TMS as the internal standard. Elemental analysis was performed on Perkin-Elmer 240 instrument. Mass spectra were determined with MALDI-TOF-MS. IR spectra were recorded on NEXUS 870 (Nicolet) spectrophotometer in the 400–4000  $\text{cm}^{-1}$  region using a powder sample on a KBr plate.

Single crystals of the complexes **1** and **2** used in X-ray determination were obtained by slow evaporation of methanol covered with acetonitrile at room temperature. X-ray diffraction data of them were collected on a Bruker Smart 1000 CCD area detector diffractometer. Both of the radiation sources were Mo  $K\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ). Empirical absorption correction was applied to the data. The structures were solved by direct methods and refined by full-matrix least-squares methods on  $F^2$ . All the nonhydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using the full matrix least-squares procedure. The hydrogen atom positions were geometrically idealized and generated in idealized positions and fixed displacement parameters. Cambridge Crystallographic Data Centre (CCDC) as supplementary publication numbers CCDC-974956 (for **1**), 974957 (for **2**).

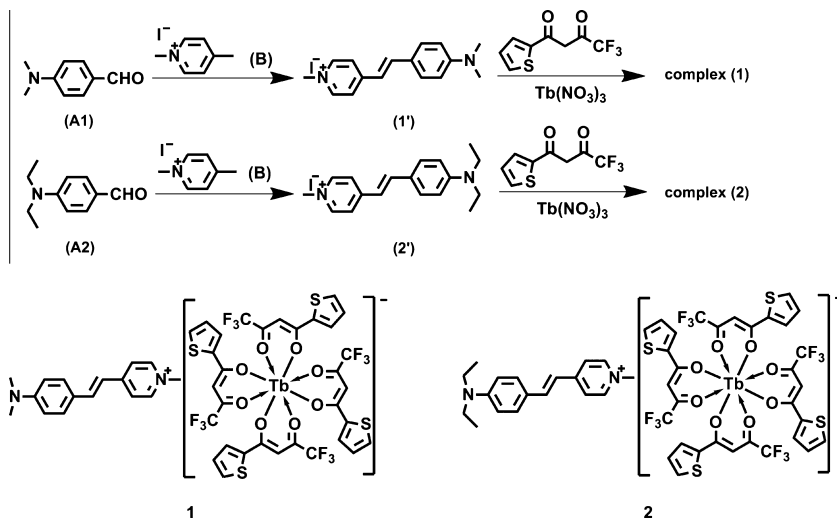
Electronic absorption spectra were obtained on a UV-265 spectrophotometer. Fluorescence measurements were performed using a Hitachi F-7000 fluorescence spectrophotometer.

Two-photon absorbing active were measured using femtosecond laser pulse and Ti: sapphire system (680–1080 nm, 80 MHz, 140 fs, Chameleon II) as the light source. All measurements were carried out at room temperature.

### Synthesis

#### Preparation of 4-(N,N-diethylamino)benzaldehyde (**A2**)

4-(N,N-diethylamino)benzaldehyde was synthesized according to the literature method [43]. At room temperature, the compound is pale yellow solid. Yield 90%. Mp: 42 °C. IR (KBr,  $\text{cm}^{-1}$ ) 2974 (m), 1665 (s), 1598 (s), 1566 (m), 1528 (s), 1470 (m), 1409 (s), 1357 (s), 1330 (m), 1179 (s), 1002 (w), 839 (m), 591 (w);  $^1\text{H}$  NMR (400 MHz,



Scheme 1. Synthesis route of **1** and **2**.

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