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Highly Selective Recognition on Enatioselective of R(+) and S(−)-1,1-Bi(2-Naphthol) Using of Eu(dap)₃ Complex as Photo Probe

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Abstract The chiral recognition phenomenon was observed in enantioselective and excited-state energy transfer processes. Based on bimolecular luminescence quenching kinetics for a system containing chiral molecules, the quenching efficiency was evaluated by Stern-Volmer equation for a system containing a chiral R(+) and S(−) resolved quencher species. The utility of this methodology is confirmed by examining the enantio-selective excited-state quenching between Eu(dpa)₃ complex (where dpa = pyridine-2,6-dicarboxylate) acting as the energy donor to R(+)-1,1-Bi(2-Naphthol) and S(−)-1,1-Bi(2-naphthol) as the energy acceptor was studied in solution. The results of this study confirm the utility of luminescence measurements as a probe of chiral discriminatory behavior.

Keywords Chiral recognition · Stern-Volmer quenching kinetics · Luminescence quenching

Introduction

Luminescence from lanthanide complexes has been of interest for many years due to their intense emission peaks (<10 nm full width at half-maximum) in the visible and near-infrared region under UV excitation [1]. Due to the lanthanides' electronic structure, their complexes have unique optical properties, including luminescence lifetimes that range from micro- to milliseconds, and sharp emission bands whose width at half-height (fwhm) rarely exceed

10 nm [2–4]. This is much narrower than the typically broad fluorescence arising from organic molecule or Cd/Se nanoparticles [5].

The lanthanide *f-f* transitions are Laporte forbidden [6], the molar absorptivity is very low. The typical strategy to circumvent this is to increase the luminescence excitation by coordinating the luminescent lanthanide ion to a chromophore, which acts as an antenna to effectively transfer light energy to the metal [7, 8].

In order to form luminescent lanthanide complexes with PL activity, chiral complexes have been developed where the coordination geometry around the lanthanide is well-defined and controllable, which enables finetuning of the photophysical properties [9]. Both enantiomers of 1,1′-bi-2-naphthol are widely used for various applications: 1) chiral inducing agents for catalytic, asymmetric reactions such as the Diels-Alder reaction, ene reaction, or as Lewis acids; 2) enantioselective reduction of ketones; 3) synthesis of chiral macrocycles and other interesting compounds. Previously reported resolutions include: 1) making a cyclic phosphate of binaphthol, then resolution and subsequent reduction to release the pure binaphthol; 2) using enzymatic hydrolysis of the diester of binaphthol; and 3) forming inclusion complexes with suitable compounds [10].

The mechanism of intermolecular recognition phenomena exhibited between chiral molecules are a topic of significant importance in biology and chemistry. Chiral recognition phenomena can be exhibited by static recognition interactions, which include long-lived binding interactions between chiral species, and by dynamic recognition interactions, which include short-lived chiral discriminatory interactions. Exploration of these phenomena has received considerable attention with respect to experimental characterization and theoretical rationalization of chiral discriminatory behavior. Efforts to join theory with experiment have

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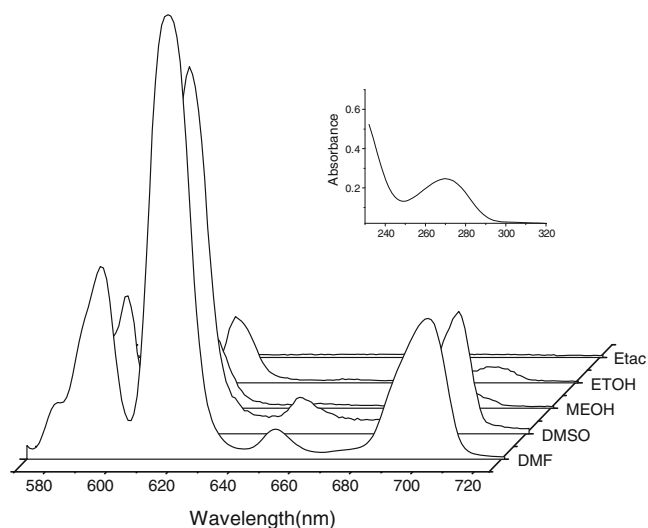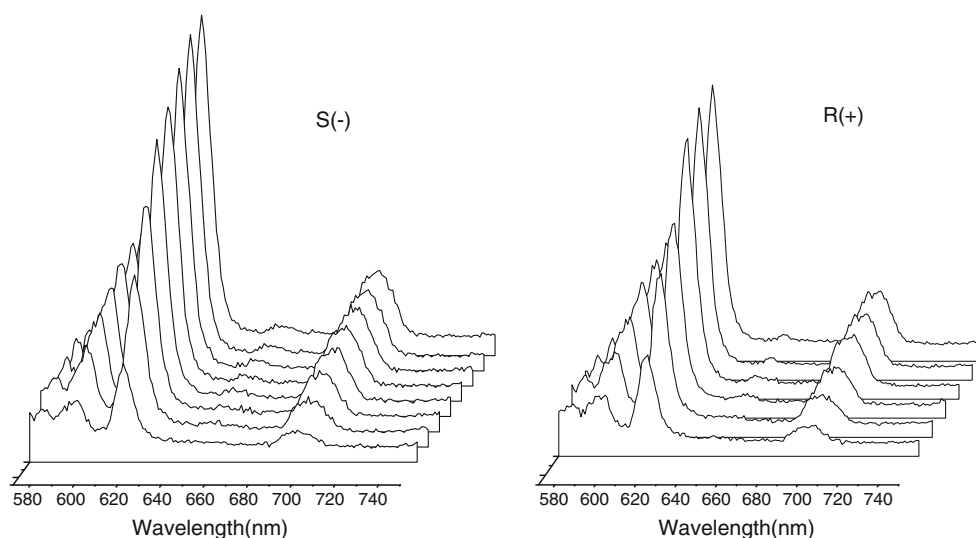Cairo, Egypt
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Fig. 1 Photoluminescence spectra of Eu(dap)$_3$ in different solvents at λ_{ex}=340 nm and insertion fig of absorption spectrum of Eu(dap)$_3$

Experimental

Instruments

All fluorescence measurements were carried out on Shimadzu RF5301 Spectrofluorophotometer in the range (290–750 nm). The absorption spectra were recorded with a Unicam UV-Visible double-beam spectrophotometer from Helios Company. It employs a Tungsten filament light source and a Deuterium lamp, which have a continuous spectrum in the ultraviolet region. The spectrophotometer is equipped with a temperature-controller cell holder.

Materials and Reagents

All chemicals and solvents were used analytical-reagent of the highly grade. Pure standards of R(+)-1,1-Bi(2-Naphthol) and S(−)-1,1-Bi(2-naphthol) were purchased from Aldrich. Distilled water and pure grade solvents from (Aldrich) were used for the preparation of all solutions and during the all measurements. The stock solutions of the aqueous Eu(dpa)$_3$ complex was prepared by the reaction of EuCl$_3$.6H$_2$O with molar ratio 1:3 from dipicolinic acid (2,6-pyridine dicarboxylic acid). The resulting solution was brought to pH 7.2 by titration with a 0.1 M aqueous solution of NaOH [12]. All experiments are carried out at room temperature.

met with mixed success. In systems exhibiting static recognition phenomena, chiral recognition can be rationalized at a phenomenological level, in terms of steric/electrostatic lock-and-key models. These models can be used with some success when the interacting molecules have highly differentiated stereochemical structures. These "lock-and-key" models, however, do not address contributions to chiral recognition from dynamic electronic interactions of the kinds found in intermolecular energy-transfer process or in stereoselective electron transfer reactions. These dynamic electronic processes are notoriously difficult to model and are elusive to direct measurement [11]. This study presents luminescence methodology to determine the magnitude of the chiral discriminatory behavior observed in enantioselective energy transfer interactions.

Results & Discussion

The luminescence spectra of Eu(dpa)$_3$ complex was obtained by excitation at 340 nm at room temperature. The photoluminescence spectra of Eu(dpa)$_3$ complex was measured in different solvents at λ_{ex}=340 nm. One strong and medium

Fig. 2 Photoluminescence spectra of Eu(dap)$_3$ in the presence of S(−) and R(+)1,1-Bi (2-naphthol) acting as a quencher species at λ_{ex}=340 nm

Fig. 3 Estimation of the Stern Volmer constant, critical conc. and the apparent critical radius in case of Eu(dap)$_3$ complex using Stern-Volmer plot for S(−) and R(+)1,1-Bi(2-naphthol) species
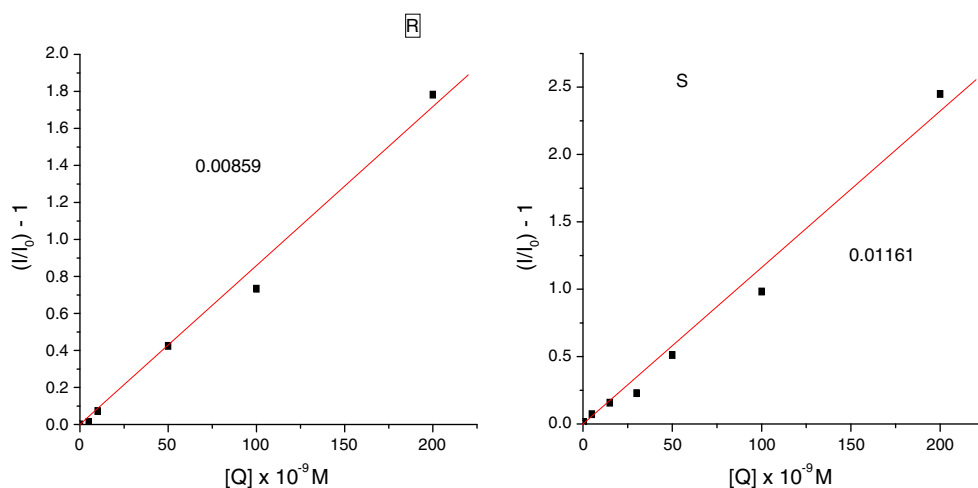
emission bands, separately corresponding to electric dipole $^5D_0 \rightarrow ^7F_2$ transition (615 nm) and magnetic dipole $^5D_0 \rightarrow ^7F_1$ transition (592 nm). The unquenched luminescence spectra were unique to Eu(dpa)$_3$ and agree with previously published results (Fig. 1) [11, 13–15].

Upon addition of either R(+) and S(−) as pure quencher species, the luminescence spectra changed only with regard to the luminescence intensity of each transition. Several additions of quencher were made to the luminophore solution to obtain the decrease in luminescence intensity as a function of quencher concentration shown in (Fig. 2).

The Stern-Volmer ratio *(Io/I)* was plotted as a function of quencher concentration shown in (Fig. 3).

The chiral discriminatory interactions between enantiomers and luminphore species can be explored by Stern-Volmer quenching measurements. The interaction between enantiomerically and luminophore yields the linear Stern-Volmer equation, where the quenching rate constant *(k$_q$)* is the average of the two types of quenching interactions. The same type of analysis may be applied to the case where the quencher species is present in an enantiomerically excess, resulting in the chiral discriminatory Stern-Volmer equation.

The quenching efficiency was evaluated by Stern-Volmer constant (K$_{SV}$). Quenching plots are constructed according to the following Stern-Volmer Eq. 1 [16]

$$(I_0/I) - 1 = K_{sv}[Q] \qquad (1)$$

Where, I$_o$ and I are the luminescence intensities of Eu(dap)$_3$ complex in absence and in presence of the quencher, respectively, [Q] is the concentration of the quencher, and κ_{sv} called Stern-Völmer constant. If the luminescence intensities are plotted against the concentration of the quencher, the slope of the fitted data is equal to the Stern-Völmer constant. Moreover, one over κ_{sv} equal C_O (a critical concentration), which defines as the acceptor concentration at which the

donor luminescence quanta yield falls by a factor 0.5.

$$C_O = 1/\kappa_{sv} \qquad (2)$$

Using Eq. 3 one can calculate R$_o$

$$R_o = 7.35C_O^{-1/3} \qquad (3)$$

Where the Förster critical distance (**R(0)**) is defined as the acceptor-donor separation radius for which the transfer rate equals the rate of donor decay (de-excitation) in the absence of acceptor. In other words, when the donor and acceptor radius (**r**) equals the Förster distance, then the transfer efficiency is 50%. At this separation radius, half of the donor excitation energy is transferred to the acceptor via resonance energy transfer, while the other half is dissipated through a combination of all the other available processes, including fluorescence emission. From Table 1, the mechanism between luminophore and quencher species is dipolar-dipolar interaction (R0<10 nm) [17].

Conclusion

The goal of this study was to develop and test a steady state luminescence technique to probe chiral discriminatory

Table 1 Stern-Volmer constant, (K$_{sv}$), critical concentration, (C$_o$), and critical radii, (R$_0$) for quenching of luminescence of Eu(dap)$_3$ complex with different concentration of S(−) and R(+)1,1-Bi(2-naphthol)

	K$_{sv}$ (mol^{-1} l)	C$_{o1/2}$ (mol/l)	R$_o$ (Å)±SD*
S(−)1,1-Bi(2-naphthol)	0.011	90.9	1.65±0.242
R(+)1,1-Bi(2-naphthol).	0.009	111.1	1.55±0.065

SD* Standard deviation.

interactions between various molecules or complexes. In the presence of an enantiomerically quencher species, the mechanistic analysis yields the expected Stern-Volmer equation. However, in the presence of an enantiomerically resolved quencher species. The experimental data obtained confirms the utility of this methodology for determining the magnitude of chiral recognition between Eu(dpa)$_3$ luminophore and quencher species, with good agreement with previously published results [4, 11]. The work presented here provides a foundation to explore chiral recognition phenomena without the use of chiroptical techniques. This methodology opens luminescence studies of chiral recognition to luminescent transition metal complexes or to fluorescent organic molecules that lack the large absorption or emission dissymmetry factors that are required to observe chiroptical spectro-scopic properties.

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