



Crystal structures, two-photon excited fluorescence and bioimaging of Zn(II) complexes based on an extended 2,2'-bipyridine ligand



Feng Jin^a, Wenchao Shu^a, Xianpeng Yu^a, Yue Zhang^a, Lin Sun^a, Yong Liu^c, Dongliang Tao^a, Hongping Zhou^{b,*}, Yupeng Tian^b

^a College of Chemistry and Material Engineering, Fuyang Normal College, Fuyang 236037, PR China

^b College of Chemistry and Chemical Engineering, Anhui University, Hefei 230039, PR China

^c College of Life Science, Fuyang Normal College, Fuyang 236037, PR China

ARTICLE INFO

Article history:

Received 7 May 2015

Received in revised form

26 May 2015

Accepted 31 May 2015

Available online 10 June 2015

Keywords:

Zn(II) complex

Two-photon excited fluorescence

Two-photon absorption cross-section

Crystal structure

Structure–property relationship

Bioimaging

ABSTRACT

Two new luminescent zinc complexes based on a donor– π –bridge–acceptor organic ligand bearing a diphenylamine donor group and 2,2'-bipyridine acceptor group were prepared and characterized. The structures of the dyes were solved by single crystal X-ray diffraction analysis. Research has shown that the dyes exhibit superior two-photon excited fluorescence with the large two-photon absorption cross-section values of over 630 GM. The structure–property relationships were detailed through X-ray crystallography. Results of living cell imaging experiments show the potential of these dyes in fluorescence microscopy bioimaging.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

In recent years, inorganic–organic hybrid materials with superior two-photon excited fluorescence (TPEF) and large two-photon absorption (TPA) cross-section continue to be the subject of very active research due to their potential applications as two-photon optical materials in several areas, such as fluorescence imaging, photodynamic therapy, photoswitching devices and 3-D data storage [1–4]. Up to now, more organic two-photon absorption materials have been extensively studied. The organic TPA materials with large TPA cross-sections often possess a rigid, conjugated, planar structure with π -centers and electron-donor and/or electron-acceptor moieties at the terminal sites [5–7]. The syntheses of such molecules often require significant synthetic skills and generally afford very low yields of the desired products. Compared with the organic TPA materials, the inorganic–organic hybrid materials often show many unique advantages, such as better physical and chemical stability and potentially higher yield and easier synthesis. In addition, through metalation, the flexibility

of the organic ligand can be reduced and the photochemical stability of it might be enhanced [8,9]. In coordination compounds, the metal ions can act either as a multidimensional template for increasing the molecular number density of two-photon active components, or as an important structural control on the intramolecular charge transfer process, leading to a large two-photon absorption cross-section [10]. The investigations on such TPA complexes have revealed that control of the functional organic ligands and the metal ion center, which are interconnected, is of crucial importance to optimize the physical properties of the complexes [11].

Zn(II), being a bioavailable metal which widely exists in metalloenzymes and has a closed-shell electronic configuration of $3d^{10}4s^0$ anticipates to produce fluorescence characteristics dependent on the ligands. Therefore, luminescent Zn complexes are of increasing interest in photochemistry, luminescence sensors, and optical probes in biological studies [2,9,12]. In this work, 2,2'-bipyridyl group as electron acceptor moiety was incorporated into a diphenylamine electron donor through a π -conjugating spacer, a new fluorescent donor– π –bridge–acceptor (D– π –A) structural organic ligand, 6-phenyl-4'-(4-[4-(diphenylamino)styryl]phenyl)-2,2'-bipyridine (**L**) was obtained. By self-assembly of

* Corresponding author. Tel.: +86 551 5108151; fax: +86 551 5107342.

E-mail address: zhpzhp@263.net (H. Zhou).

the ligand with zinc(II) salts, two Zn(II) complexes ZnBr₂L (**1**) and [ZnL₂]₂·CH₂Cl₂ (**2**) with superior two-photon excited fluorescence (TPEF) and high two-photon absorption (TPA) cross-section values were successfully prepared. The results of living cell imaging experiments demonstrate the potential of these complexes in fluorescence microscopy bioimaging.

2. Experimental section

2.1. General procedures

All commercially available chemicals are of analytical grade. Every solvent was purified by conventional methods beforehand. Scheme 1 depicts the synthetic pathways we used to prepare dyes **1** and **2**. The intermediates and **L** were synthesized according to previously reported procedures [13]. IR spectra were recorded with a Nicolet FT-IR NEXUS 870 spectrometer (KBr discs) in the 4000–400 cm⁻¹ region. Elemental analyses were carried out on Perkin–Elmer 240 analyzer. The X-ray diffraction measurements were performed on a CCD area detector using graphite monochromated MoK α radiation ($\lambda = 0.71069 \text{ \AA}$) at 298 (2) K. Intensity data were collected in the variable ω -scan mode. The structures were solved by direct methods and difference Fourier syntheses. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were introduced geometrically. Calculations were performed with SHELXTL-97 program package. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC: 995453 (for **1**), 978278 (for **2**).

2.2. Optical measurements

The one-photon excited fluorescence (OPEF) spectra measurements were performed using a Hitachi F-7000 fluorescence spectrophotometer. In the measurements of excitation and emission spectra, the pass width is 5 nm.

Two-photon absorption cross-sections (δ) of the samples were obtained by two-photon excited fluorescence method [14] at femtosecond laser pulse and Ti: sapphire system (680–1080 nm, 80 MHz, 140 fs) as the light source. The sample was dissolved in DMF at a concentration of $1.0 \times 10^{-3} \text{ mol L}^{-1}$. The intensities of TPEF spectra of the reference and the sample were determined at their excitation wavelength. Thus, TPA cross-section of samples was determined by Eq.:

$$\delta = \delta_{ref} \frac{\Phi_{ref} c_{ref} n_{ref} F}{\Phi c n F_{ref}}$$

where the *ref* subscripts stand for the reference molecule (here fluorescein in the aqueous NaOH solution (1 mol L^{-1}) at concentration of $1.0 \times 10^{-3} \text{ mol L}^{-1}$ was used as reference). δ is the TPA cross-sectional value, *c* is the concentration of the solution, *n* is the refractive index of the solution, *F* is the TPEF integral intensities of

the solution emitted at the exciting wavelength, and Φ is the fluorescence quantum yield. The δ_{ref} value of reference was taken from the literature [15].

2.3. Cell culture and incubation

NIH/3T3 cells were seeded in 6 well plates at a density of 2×10^5 cells per well in cell-culture media (10% FCS: 90% DMEM) and grown for 96 h. The dyes were dissolved in DMSO at concentration of $1.0 \times 10^{-3} \text{ mol L}^{-1}$ and diluted with cell-culture media to a working concentration of 40 $\mu\text{L/mL}$. The cells were incubated with the dyes and maintained at 37 °C in an atmosphere of 5% CO₂ and 95% air for 0.5 h. The cells were then washed with cell-culture media (3 \times 3 mL per well) before used.

2.4. Fluorescence imaging

NIH/3T3 cells were luminescently imaged on a TCS-SP5 II, Leica confocal laser scanning microscope using magnification 40 \times for monolayer cultures. Image data acquisition and processing was performed using Leica LAS-AF and Image J. Laser used 405 diode (UV), and emission bandwidth was 500–550 nm.

2.5. Synthesis

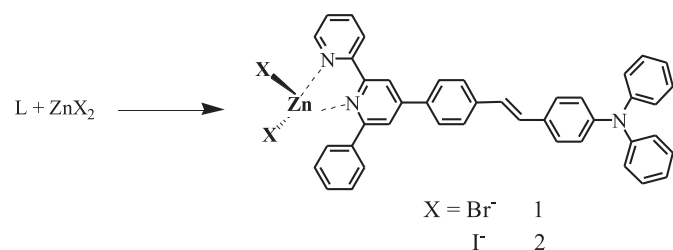
Synthesis of complex ZnLBr₂ (dye 1): A clear methanol solution (20 mL) of ZnBr₂ (1 mmol, 0.22 g) was carefully layered onto a solution of **L** (1 mmol, 0.58 g) in dichloromethane (20 mL). Red flake-like single crystals of **1** suitable for single crystal X-ray diffraction analyses were obtained by slow interlayer diffusion. Yield: 0.60 g (76%). mp > 300 °C. Anal. Calcd. (%) for ZnBr₂C₄₂H₃₁N₃: C, 62.83; H, 3.89; N, 5.23. Found (%): C, 62.61; H, 3.61; N, 5.55. IR $\nu(\text{cm}^{-1})$: 2362, 2337, 1588, 1486, 1540, 1325, 1273, 1172, 1026, 792, 771, 749, 721, 697, 536.

Synthesis of complex [ZnL₂]₂·CH₂Cl₂ (dye 2): A clear methanol solution (20 mL) of ZnL₂ (1 mmol, 0.32 g) was carefully layered onto a solution of **L** (1 mmol, 0.58 g) in dichloromethane (20 mL). Red rod-like single crystals of **2** suitable for single crystal X-ray diffraction analyses were obtained by slow interlayer diffusion. Yield: 0.76 g (82%). mp > 300 °C. Anal. Calcd. (%) for C₈₅H₆₄Cl₂I₄N₆Zn₂: C, 56.88; H, 3.57; N, 4.70. Found (%): C, 56.60; H, 3.22; N, 4.46. FT-IR (KBr, cm⁻¹): 2917, 1795, 1585, 1486, 1368, 1327, 1274, 1449, 1168, 1025, 876, 697, 585.

3. Results and discussion

3.1. Description of X-ray crystal structures

The structures of dyes **1** and **2** were confirmed by X-ray crystallography. The molecular structures have been depicted in Figs. 1 and 2. Details of the crystal parameters, data collections and



Scheme 1. Synthetic route to dyes **1** and **2**.

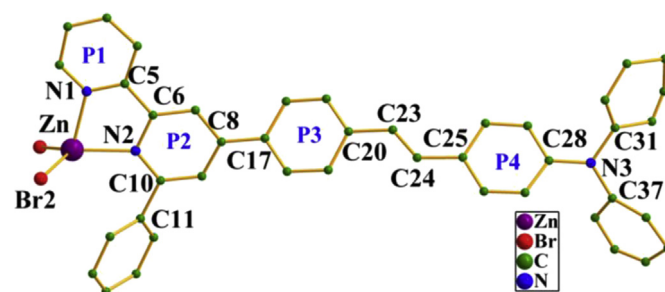


Fig. 1. Molecular structure of dye **1**. Hydrogen atoms are omitted for clarity.

Download English Version:

<https://daneshyari.com/en/article/175594>

Download Persian Version:

<https://daneshyari.com/article/175594>

[Daneshyari.com](https://daneshyari.com)