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Enhanced two-photon excited fluorescence of mercury complexes with a conjugated ligand: Effect of the central metal ion

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ABSTRACT

Based on the chelation of 6-phenyl-4'-(4-[4-(diphenylamino)styryl]phenyl)-2,2'-bipyridine (**L**) to Hg(II) ions, two luminescent coordination complexes HgBr₂L (**1**) and HgL₂ (**2**) were prepared. Compared with the free ligand, the complexes exhibit enhanced two-photon excited fluorescence and larger two-photon absorption cross-section values. Time-dependent density functional theory calculations were carried to investigate the influence of central metal ion on the characteristic of charge transition of the complexes. The results indicated that the complexation of the ligand with Hg(II) ion causes stronger intramolecular charge transfer, leading to enhanced two-photon absorption of the complexes.

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1. Introduction

Recently, optical materials with excellent two-photon excited fluorescence (TPEF) or large two-photon absorption (TPA) cross-section (δ) have attracted considerable interest due to their potential applications as two-photon optical materials in several areas, such as photodynamic therapy [1], fluorescence imaging [2], 3-D data storage [3], optical power limiting [4] and up-converted lasing [5], etc. The wide range of applications have generated a demand for new materials with high two-photon absorption cross-sections [6,7]. However, the small two-photon absorption cross-section values often limit the widespread utility of the materials [8–10]. In the past few decades, researchers have tried to design and synthesize TPA materials with large TPA cross-sections and many strategies have been proposed to improve TPA response, such as connecting electron acceptor (A) and donor (D) groups symmetrically or unsymmetrically through π -conjugating spacers to form A- π -A, D- π -D, or D- π -A structures and building of multi-branched molecules, which can significantly enhance TPA cross-section values by increasing chromophore density of the molecules and the cooperative enhancement effect among the chromophores [11–13].

Compared with the organic TPA materials, coordination complexes show many unique advantages, such as easier synthesis, higher yield, better physical and chemical stability, etc. [14–17].

Most importantly, in coordination complexes, 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 an enhanced two-photon absorption cross-section [18–20]. In addition, metal center can induce a stronger intra-ligand charge-transfer (ILCT) transition to improve TPA cross section values [21], and a low-energy metal ligand charge-transfer transition (MLCT) may occur to effect TPA cross-section values [22,23].

2,2-Bipyridine and its derivatives are an important kind of ligands in the fields of coordination chemistry. They exhibit excellent optical properties and extremely strong binding affinity towards most transition metal ions [24]. In our previous work, a D- π -A structural organic compound with excellent two-photon excited fluorescence and large TPA cross-section, 6-phenyl-4'-(4-[4-(diphenylamino)styryl]phenyl)-2,2'-bipyridine (**L**) has been designed and prepared [25]. As continuous efforts to explore new fluorescence materials, new coordination complexes containing 6-phenyl-4'-(4-[4-(diphenylamino)styryl]phenyl)-2,2'-bipyridine were prepared. Hg(II) possesses a closed-shell electronic configuration of d¹⁰, which makes it be particularly suitable for construction of fluorescence coordination complexes [26]. Therefore, by chelate reaction of **L** with mercury(II) ion, two Hg(II) complexes HgBr₂L (**1**) and HgL₂ (**2**) with superior two-photon excited fluorescence and large two-photon absorption cross-section were obtained. Compared with the free ligand, the complexes exhibit enhanced two-photon excited fluorescence emission and increased TPA cross-section. The excellent TPEF and large

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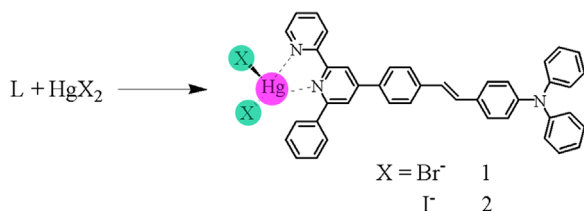
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TPA cross-section demonstrate the values of them in two-photon optical materials.

2. Experimental section

2.1. General procedures

All commercially available chemicals are of analytical grade. Every solvent was purified as conventional methods beforehand. Scheme 1 depicts the synthetic pathway we used to prepare the complexes. The ligand was synthesized according to our previously reported procedures [25]. 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-



Scheme 1. Synthetic route to complexes 1 and 2.

Elmer 240 analyzer. ^1H NMR spectra were recorded on a Bruker AV 600 spectrometer with TMS as internal standard.

Time-dependent density functional theory (TD-DFT) calculations on the complexes and the free ligand were carried out using Gaussian 03 program. Geometry optimization of singlet–singlet excitation energies were carried out with a basis set composed of 6-31G(d) for C, N, and H atoms and the LANL2DZ basis set for Hg, Br and I atoms.

2.2. Optical measurements

The one-photon absorption (OPA) spectra were recorded on a SPECORD S600 spectrophotometer. 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. OPA and OPEF were measured in five organic solvents of different polarities with the concentration of $1.0 \times 10^{-5} \text{ mol L}^{-1}$. The quartz cuvettes used are of 1 cm path length. The absolute fluorescence quantum yield (Φ) values were determined using an integrating sphere.

Two-photon absorption cross-sections (δ) of the samples were obtained by two-photon excited fluorescence method [27] 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

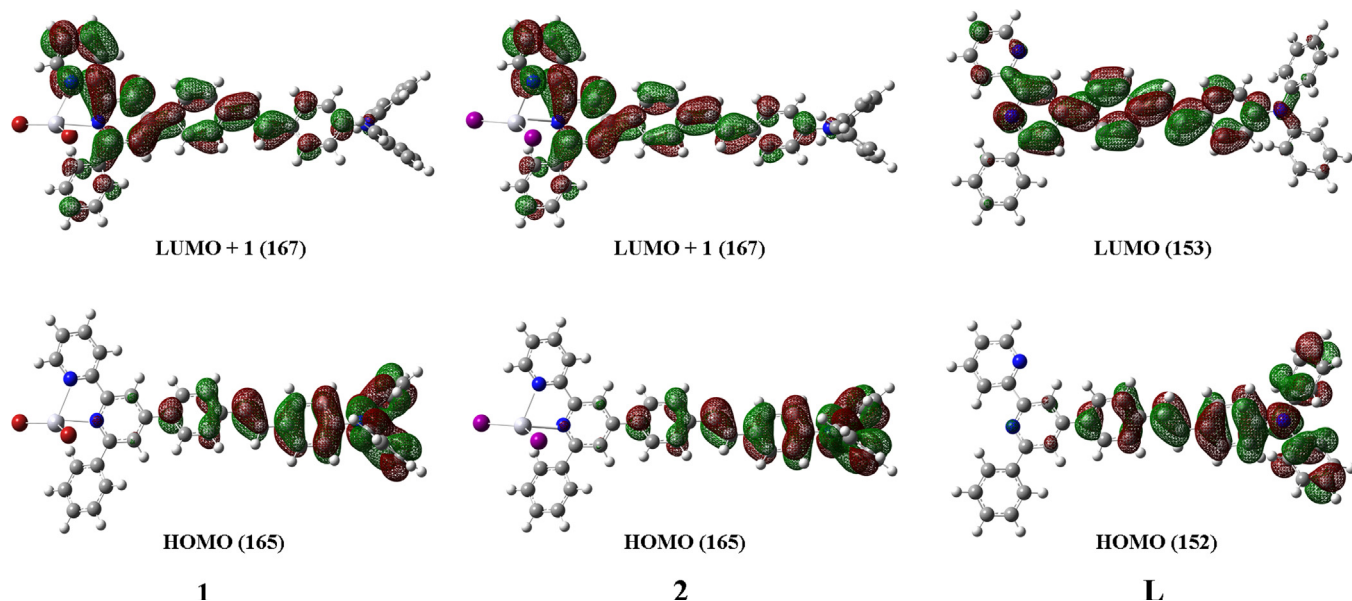


Fig. 1. The electron cloud distribution of frontier molecular orbitals of 1, 2 and L.

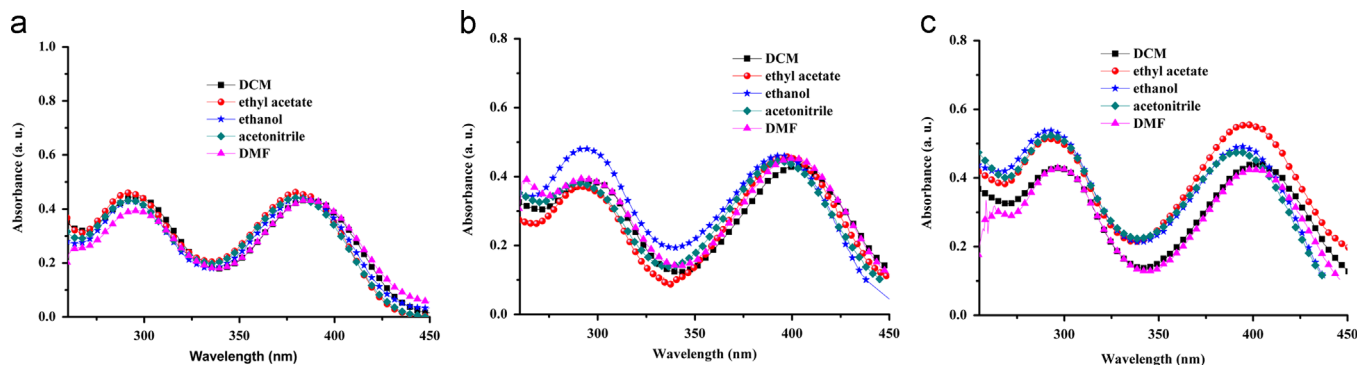


Fig. 2. Linear absorption spectra of L (a), complexes 1 (b) and 2 (c) in five organic solvents.

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