

## Solvent effects on one- and two-photon optical properties of a novel 2, 2':6', 2''-terpyridine-based chromophore

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Received 20 August 2012; Accepted (in revised version) 15 September 2012

Published Online 30 August 2013

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**Abstract.** At *ab initio* level, time-dependent hybrid density functional theory and response theory have been applied to study the solvent effect on the geometrical and electronic structure as well as one- and two-photon absorption (TPA) properties of 2,2':6',2''-terpyridine-based chromophore L. It is found that solvatochromic shift of charge-transfer (CT) appears nonmonotonic behavior with regard to the polarity of solvent. Besides, the one-photon absorption (OPA) strengths are enlarged slightly and are more dependent on the optical dielectric constant. The TPA cross sections are enhanced when considering solvent effect compared to that in gas phase and the TPA cross sections show an increasing trend with the increase of solvent polarity. All the theoretical results are in reasonable agreement with experimental data.

**PACS:** 31.15.A-, 31.70.Dk, 82.50.Pt, 42.65.-k

**Key words:** solvent effect, two-photon absorption, response theory, organic compound

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## 1 Introduction

Organic materials with large two-photon absorption (TPA) cross sections have been explored experimentally and theoretically during the last two decades for their various applications including photodynamic therapy[1], optical limiting[2,3], three-dimensional (3D) optical data storage[4], upconverted lasing[5] and 3D-microfaction[6]. For all these applications, specifically designed organic molecules with large TPA cross-sections are highly desirable. Thus, improving the TPA cross-section values of compounds is a fundamental issue in this field. In recent years, one has found that factors such as the coplanarity, the center properties, the symmetrical or asymmetrical arrangement of electron-donor (D) and electron-acceptor (A) attached to the center and their strength to push

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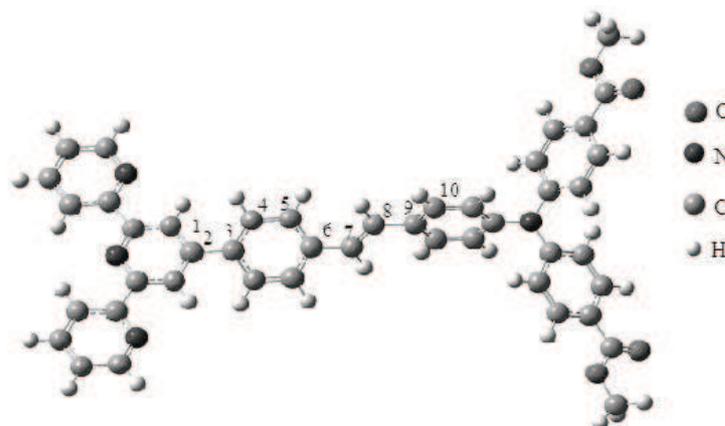


Figure 1: Optimized geometry of molecule L in gas phase.

and pull electrons, conjugation length and the molecular dimensionality have a significant impact on TPA cross-sections[7,8]. In addition, proper water solubility, good biocompatibility and photo stability should also be considered in order to satisfy special requirements.

Although modulating molecular structure has been the most effective way to change the TPA cross sections of molecules, the influence of the solvent on electronic and geometrical structures of compounds is also an important aspect to affect their optical properties since almost all the experimental measurements for organic molecules have been carried out in the liquid phase or in solutions, and some theoretical investigations have been carried out[9-11]. In this work, we have carried out the theoretical calculation for two-photon chromophore synthesized by Liu et al. recently[12]. The object of study is shown in Fig. 1. The molecule L is a compound which can be seen as typical D- $\pi$ -A style including three parts: 2,2':6',2''-terpyridine(acceptor),  $\pi$ -electron bridge and diphenylamine(donor) with methylformate group for the purpose of potential coordinating function after its hydrolysis. Herein, the solvent effects on one- and two-photon absorption properties are numerically calculated at the density functional theory (DFT) level. The computational scheme presented in this work is general and can be applied to other charge-transfer systems.

## 2 Computational detail

The transition probability of one photon absorption can be described by the oscillator strength

$$\delta_{op} = \frac{2\omega_f}{3} \sum_{\alpha} |\langle 0 | \mu_{\alpha} | f \rangle|^2 \quad (1)$$