

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

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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.

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

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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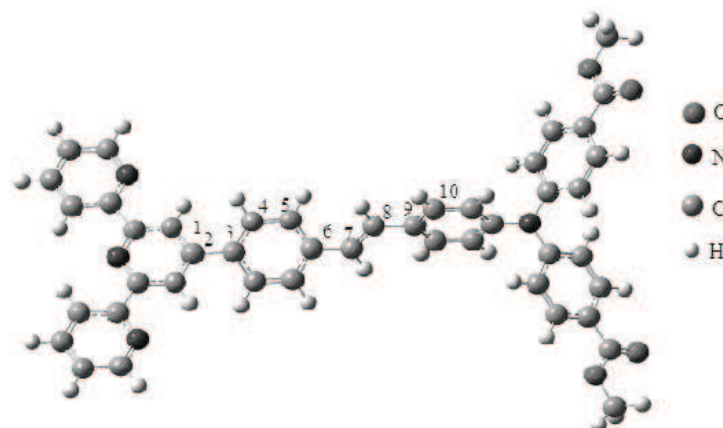


Figure 1: Optimized geometry of molecule L in gas phase.

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- π -A style including three parts: 2,2':6',2''-terpyridine(acceptor), π -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

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

Where $|0\rangle$ and $|f\rangle$ denote the ground state and the final state separately, ω_f represents the corresponding excitation energy, and μ_α is the Cartesian component of the electronic dipole moment operator. The summation is performed over the molecule x , y , and z axes: $\alpha \in \{x, y, z\}$.

The two-photon absorption cross-section that can be directly compared with the experimental results is defined as

$$\sigma_{tp} = \frac{(2\pi)^3 a_0^5 \alpha}{c_0 \pi} \times \frac{\omega^2 g(\omega)}{\Gamma_f} \delta_{tp} \quad (2)$$

Here a_0 is the Bohr radius, c_0 is the speed of light, α is the fine structure constant, ω is the photon frequency of the incident light, and $g(\omega)$ denotes the spectrum line profile, which is assumed to be a δ function here, Γ_f is the lifetime broadening of the final state, which is commonly assumed to be 0.1 eV, and δ_{tp} is orientation average value of the two-photon absorption probability in gas and solution, which is written as follows,

$$\delta_{tp} = \frac{1}{30} \sum_{\alpha\beta} \left[F \times S_{\alpha\alpha} \times S_{\beta\beta}^* + G \times S_{\alpha\beta} \times S_{\alpha\beta}^* + H \times S_{\alpha\beta} \times S_{\beta\alpha}^* \right] \quad (3)$$

where F , G , and H are coefficients dependent on the polarization of the light. For the linearly polarized light, F , G and H are 2,2,2, for the circularly case, they are -2,3,3. $S_{\alpha\beta}$ is the two-photon transition matrix element. For the absorption of two photons with the same frequency $\omega_f/2$ it can be written as

$$S_{\alpha\beta} = \sum_i \left[\frac{\langle 0 | \mu_\alpha | i \rangle \langle i | \mu_\beta | f \rangle}{\omega_i - \omega_f/2} + \frac{\langle 0 | \mu_\beta | i \rangle \langle i | \mu_\alpha | f \rangle}{\omega_i - \omega_f/2} \right] \quad (4)$$

where ω_i and ω_f denote the excitation frequency of the intermediate state $|i\rangle$ and final state $|f\rangle$ respectively, $\alpha, \beta \in \{x, y, z\}$ and the summation goes over all the intermediate states including the ground state $|0\rangle$ and the final state $|f\rangle$.

The compounds' geometries were fully optimized using the Gaussian09 package[13] at Hatree-Fork (HF) level. The calculation of one-photon absorption (OPA) is carried out by use of TD-DFT theory, which is implemented by the Gaussian09 package, too. The approach to calculate TPA cross section of molecules is quadratic response theory as implemented in the Dalton package[14] that can provide an analytical solution for the TPA cross section. The 6-31G* basis set are used for all the calculations. To simulate the solvent effect on the electronic structure, OPA and TPA properties, the sophisticated polarized continuum model (PCM) model is applied. The charge density differences between CT and ground states are visualized by Molekel program [15].

Table 1: Selective dihedral angles (degree) and bond lengths (angstrom) of the optimized geometries for molecule L in different solvents.

Solvent	ϵ_0	C ₁ -C ₂ -C ₃ -C ₄	C ₅ -C ₆ -C ₉ -C ₁₀	C ₆ -C ₇	C ₇ -C ₈	C ₈ -C ₉	BLA
Gas	1	40.7383	46.1071	1.4763 ^a	1.3280 ^b	1.4762 ^c	0.8133
C ₆ H ₁₂	2.023	40.5539	42.7028	1.4765 ^a	1.3283 ^b	1.4764 ^c	0.8123
C ₆ H ₆	2.274	40.5258	42.1398	1.4766 ^a	1.3284 ^b	1.4765 ^c	0.8123
CH ₃ COOC ₂ H ₅	5.986	40.3122	37.8717	1.4767 ^a	1.3287 ^b	1.4767 ^c	0.8123
THF	7.58	39.9942	34.6059	1.4767 ^a	1.3288 ^b	1.4767 ^c	0.8123
CH ₂ Cl ₂	8.93	40.0060	34.4665	1.4767 ^a	1.3288 ^b	1.4767 ^c	0.8123
CH ₃ CN	36.64	40.0876	33.6714	1.4768 ^a	1.3290 ^b	1.4768 ^c	0.8123
DMF	37.219	40.0860	33.6525	1.4768 ^a	1.3290 ^b	1.4768 ^c	0.8123

^{a,b,c} The corresponding experimental results from Ref. [12] are 1.481, 1.224 and 1.493 Å respectively.

3 Results and discussion

3.1 Molecular structures

We optimize the molecular geometry at HF/6-31G* level. The reason why we choose HF method rather than DFT method is because the HF geometry possesses larger bond length alternation and certain torsion angles between the two central phenyl planes, thus we can get better numerical simulated results compared with experimental measurement. The geometry in gas phase is shown in Fig. 1. We also optimize L using PCM model in different solvent at the same level. Some selective dihedral angles and bond lengths of the optimized geometries in various solvents are collected in Table 1. From Table 1, one can find that the dihedral angles C₅-C₆-C₉-C₁₀ between the two π -central phenyl planes decrease when increasing the polarities of solvent, that is the planarity of molecule L becomes better with the increase of polarities of solvent. In addition, the bond length alteration (BLA) in different solvent are nearly the same, which indicate that the solvent effect have little effect on the bond length.

3.2 One-photon absorption

The excitation energies and the oscillator strengths of the excited states are calculated by the TD-DFT at B3LYP/ 6-31G* level with fully optimized geometries. PCM model is used when considering solvent effect. The excitation energy, the corresponding wavelength and the oscillator strength of the charge-transfer states in different solvents are listed in Table 2. One can find that the compound has two CT states (the first and fifth excited states) in low energy region, which correspond to the two absorption peaks of L in experimental measurement. The wavelength shows somewhat red shift compared to gas phase when considering the solvent effect. And the one-photon transition energies corresponding to the maximum OPA peaks show a nonmonotonic decrease with increas-

Table 2: Calculated oscillator strength δ_{op} (arb. units), the excitation energies E (eV), and the corresponding wavelength λ_{op} (nm) of the charge transfer states for the molecule L in different solvents. The static dielectric constant ϵ_0 and optical dielectric constant ϵ_{opt} are also reported.

Solvent	ϵ_0	ϵ_{opt}	E	λ_{op}	δ_{op}
Gas	1	1	3.22	384.50	1.03
			3.99	309.98	0.85
Cyclohexane	2.0165	2.035	3.18	389.75	1.17
			3.93	314.96	0.86
Benzene	2.2706	2.25	3.17	390.47 (360*)	1.18
			3.92	315.64 (286*)	0.86
Ethylethanoate	5.9867	1.88	3.16	391.56 (355*)	1.15
			3.91	316.81 (285*)	0.86
THF	7.4257	1.9881	3.15	393.04 (356*)	1.16
			3.89	318.18 (289*)	0.87
Dichloromethane	8.93	2.0164	3.15	393.31 (356*)	1.17
			3.89	318.41 (279*)	0.87
Acetonitrile	35.688	1.806	3.15	393.30 (355*)	1.14
			3.89	318.45 (287*)	0.85
DMF	37.219	2.046	3.14	394.06 (360*)	1.16
			3.88	318.96 (290*)	0.86

* The experimental data from Ref. [12].

ing solvent polarity. The solvatochromic behavior of one-photon absorption energies of molecule L comes from the nature of its ground and excited state. This will be detailed discussed in the following part 3.4. The static dielectric constant and optical dielectric constant are also reported in Table 2. We can find that the calculated oscillator strength more depends on the optical dielectric constant.

3.3 Two-photon absorption

TPA properties of the compound are studied using PCM method at B3LYP/ 6-31G* level. The calculated TPA properties of the fourth excited state, which possesses the maximum TPA cross section, are listed in Table 3. As it is shown in Table 3, the TPA energies of molecule L performance positive solvatochromic shifts too, since they are half the OPA energies. When considering the solvent effect, TPA cross sections of compound L show large enhancement. For example, the calculated TPA cross section in DMF solvent is 2682.69 GM (1 GM= 10^{-50} cm⁴ s/photon), which is about 3.2 times larger than that in gas phase. Moreover, the change of the maximum TPA cross sections exhibits an increasing trend with the increase of solvent polarity, which accords with the order of TPA cross sections obtained from experimental measurement.

Table 3: The TPA cross section σ_{tp} ($\text{GM}=10^{-50} \text{ cm}^4\text{s}/\text{photon}$), the excitation energy E (eV), and the corresponding two-photon wavelength λ_{tp} (nm) of the S4 state for the molecule L in different solvent. The static dielectric constant ϵ_0 and optical dielectric ϵ_{opt} constant are also reported.

Solvent	ϵ_0	ϵ_{opt}	E	λ_{tp}	σ_{tp}
Gas	1	1	3.84	645.78	836.45
Benzene	2.2706	2.25	3.80	652.86	1127.70 285*
THF	7.4257	1.9881	3.78	656.68	2252.37 664*
Dichloromethane	8.93	2.0164	3.77	657.26	2387.51 995*
DMF	37.219	2.046	3.76	659.44	2682.69 1019*

* The experimental data from Ref. [12].

3.4 Charge-transfer process

Table 4 shows the net charge distribution of the terminal groups of compound L for the ground state and the first excited state in different solvents. The charge density difference between the first excited states and ground states is also listed in Table 4. We can see clearly that the CT state have higher polarity than the ground state, that induces the energy level of CT state has a lager decrease than that of ground state when considering solvent effect. The charge difference of diphenylamine group is positive, showing as electron-donor, while that of terpyridine group is negative, showing as electron-acceptor. In order to see the charge transfer process clearly, we have plotted the charge density difference between the first excited states and ground states for L in gas phase and DMF

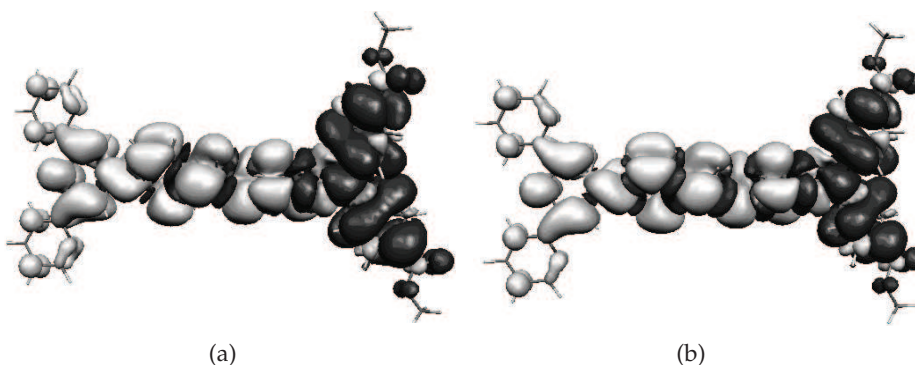


Figure 2: The charge density difference between the first excited state and the ground state of molecule L in (a) gas phase and (b) DMF solvent. The black and gray areas represent the electron loss and gain respectively.

Table 4: The net charge distribution of the electron-donor (diphenylamine) and electron-acceptor (terpyridine) for the ground state and the first excited state in different solvents.

Solvent	Radical	Q_0	Q_1	ΔQ
Gas	Diphenylamine	-0.2404	0.2934	0.5338
	Terpyridine	-0.0289	-0.1910	-0.1621
Cyclohexane	Diphenylamine	-0.2448	0.2517	0.4965
	Terpyridine	-0.0322	-0.1924	-0.1604
Benzene	Diphenylamine	-0.2454	0.2465	0.4909
	Terpyridine	-0.0327	-0.1931	-0.1604
Ethylethanoate	Diphenylamine	-0.2487	0.2178	0.4666
	Terpyridine	-0.0354	-0.2002	-0.1647
THF	Diphenylamine	-0.2493	0.2149	0.4642
	Terpyridine	-0.0357	-0.2016	-0.1658
Dichloromethane	Diphenylamine	-0.2496	0.2123	0.4619
	Terpyridine	-0.0360	-0.2028	-0.1668
Acetonitrile	Diphenylamine	-0.2506	0.2018	0.4525
	Terpyridine	-0.0372	-0.2081	-0.1709
DMF	Diphenylamine	-0.2507	0.2016	0.4523
	Terpyridine	-0.0372	-0.2082	-0.1709

solvent (see Fig. 2). The black part represents the place where electrons loss and the gray part represents the place where electrons gain. It is shown clearly that upon the excitation, the electrons move from the electron-donors to the electron-acceptors.

4 Conclusion

We have combined time-dependent hybrid density functional theory and response theory to study the solvent effect on the geometrical and electronic structure as well as one- and two-photon absorption properties of compound L on *ab initio* level. The numerical simulation shows that one photon absorption energies exhibit nonmonotonic behavior with regard to the polarity of solvents. Both the one- and two-photon absorptions are enhanced when considering solvent effect. Moreover, the OPA strengths are more dependent on the optical dielectric constant. We also have investigated the CT process. For chromophore L, the CT state own larger polarity than the ground state. Upon the excitation, the charge transfer take place and the electrons transfer from the electron-donor to electron-acceptor.

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