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Synthesis, photophysical properties and TD-DFT calculation of four two-photon absorbing triphenylamine derivatives

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In this study, linear absorption, single-photon excited fluorescence, fluorescence quantum yields, fluorescence lifetime and two-photon excited fluorescence of a series of triphenylamine derivatives (**L1**, **L2**, **L3** and **L4**) have been measured. **L1** and **L3** are D- π -A type dyes, while **L2** and **L4** are D- π -D- π -A type dyes (D = donor, A = acceptor). The investigated compounds consist of triphenylamine-bearing donor-substituted and/or systematically extended π -conjugated length, which are designed to gain insight into the effect of the ethoxyl unit and π -linkage length on the linear and nonlinear optical properties. The influence of solvent polarity on the photophysical properties was investigated. Employing time-dependent density functional theory (TD-DFT) calculations, the structure-property relationships are discussed.

triphenylamine derivatives, optical properties, structure-property relationship, TD-DFT calculation

1 Introduction

Nowadays, there have been increasing interests in organic optical materials, among which, intramolecular chargetransfer (ICT) compounds are regarded as ideal candidates due to their possible applications in optoelectronic and/or photonic fields [1, 2]. ICT molecule is characterized by an electron-donating (D) and an electron-accepting (A) group linked through π -conjugation. The optical properties of ICT molecules depend mainly on the polarizability of the electrons localized in front line molecular orbitals, which lies on the chemical structure of D and/or A group, the property of the donor and acceptor groups, the π -conjugated spacer length, and the polarizability of the solvent used for measurements [3].

When choosing electron-donating group, we are inter-

ested in triphenylamine-derivatives. Triphenylamine has been known to exhibit rigid plane, long conjugation length and good hole transporting properties [4]. Thus, triphenylamine and its derivatives have displayed promising properties in the development of light emitting [5], organic field-effect transistors (OFET) [6], photovoltaic devices [7–9] and dye-sensitized solar cells [10]. In addition, electron transfer or electron separation between the triphenylamine group and the accepting group provides this class of compounds highly anisotropic structures and results in interesting photophysical properties. Recently, our group has synthesized a number of triphenylamine derivatives with linear and/or nonlinear optical properties [11].

Considering all the aspects above, in this work, we selected a series of ICT structural triphenylamine derivatives L1–L4 (Scheme 1), including 2-(4-(diphenylamino) benzylidene)-malononitrile (abbreviated as L1), 2-(4-(4-(diphenylamino)-styryl)-benzylidene)malononitrile (abbre-

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viated as L2), 2-(4-(bis(4-ethoxyphenyl)amino)-benzylidene) malononitrile (abbreviated as L3) and 2-(4-(bis-(4-ethoxyphenyl)-amino)styryl)benzylidene)malononitrile (abbreviated as L4). In molecule L1, the triphenylamine group is employed as an electron-donating unit, the dicyano group as an electron-accepting unit, and they are linked by a vinyl bond. Based on the structure of L1, the π -electron conjugated system is enlarged by forming -C=C- to get L2, which is chosen to study the influence of the π -conjugated spacer length on the optical properties. Furthermore, ethoxvl units are introduced to the structure of L1 and L2 to form L3 and L4, respectively. The ethoxyl unit is expected to balance the charge recombination of the whole structure [12]. L1 and L2 are typical ICT compounds and have caused many interests. In 2008, Chen [13] reported the synthesis of L1. In 2009, Li [14] reported the crystal structure of L1. In 2012, Lin [15] used L2 as a colorimetric and turn-on fluorescence chemosensor for cyanide anion. However, the optical properties (especially two-photon absorption and two-photon excited fluorescence) of these compounds have not been thoroughly studied, not to say the relationship between the structure and the photophysical properties. Thus, in this study, linear and nonlinear optical properties of L1-L4 are measured. Based on TD-DFT calculations, the relationships between the structure and the optical properties are discussed.

2 Experimental

2.1 Materials and physical measurements

All chemicals were commercially available and used without further purification. The solvents, benzene, dichloro-



Scheme 1 Molecular structures of the investigated triphenylamine derivatives L1–L4.

methane (CH₂Cl₂), ethyl acetate (EtAc), tetrahydrofuran (THF) and N, N-dimethylformamide (DMF), were spectroscopic grade. The compounds were characterized by NMR, FT-IR, and elemental analysis.

Elemental analysis was performed with a Vario ELIII elemental analyzer. The ¹H NMR spectra were recorded on a Bruker Avance 400 spectrometer. FT-IR spectra were recorded on a NEXUS 870 (Nicolet) spectrophotometer in the 400–4000 cm⁻¹ region using a powder sample on a KBr plate. UV-Vis absorption spectra were recorded on a UV-3100 spectrophotometer. The fluorescence spectra were recorded on a Hitachi F-7000 fluorescence spectrophotometer. The fluorescence quantum yields (Φ) were determined against the fluorescein standard ($\Phi = 0.90$) [9]. Fluorescence lifetime measurements were carried out using an HORIBA FluoroMax-4P fluorescence spectrometer equipped with a time-correlated single-photon counting (TCSPC) card. The two-photon excited fluorescence (TPEF) spectra were measured using a mira 900-D Ti: sapphire femtosecond laser with a pulse width of 140 fs and a repetition rate of 80 MHz. Thermal analyses were performed with the Netzsch 449F3 thermal analyzer under N2 atmosphere at a heating rate of 10 °C min⁻¹.

2.2 Preparation of compound L3–L4

The detailed synthesis procedures of L3 and L4 are listed below. The synthesis procedures of other intermediates are provided in Supporting Information.

2.2.1 Preparation of L3

4-(Bis(4-ethoxyphenyl)amino)benzaldehyde (0.71 g, 2 mmol), malononitrile (0.16 g, 2.4 mmol) and K₂CO₃ (0.34 g, 2.5 mmol) were dissolved in ethanol (30 mL), refluxed overnight and monitored by TLC. Upon completion of the reaction, the mixture was cooled to room temperature, poured into CH₂Cl₂ (500 mL), washed with water (100 mL) and dried over MgSO₄. The solvent was evaporated, and the residue was purified by column chromatography of silica gel with ethyl acetate/petroleum ether mixture (1:50 v/v) as the eluent. L3 was obtained as a red solid in 57% yield. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.13 (s, 1H); 7.78(d, 2H, J = 8.8 Hz); 7.22 (d, 4H, J = 8.0 Hz); 6.99 (m, 5H); 6.67 (d, 2H, J = 8.8 Hz); 4.00 (m, 4H); 1.33 (t, 6H, J = 6.8 Hz). FT-IR (KBr cm⁻¹): 2978, 2922 (m), 2216 (C≡N, m), 1712 (m), 1591 (s), 1510 (s), 1268 (s), 1238, 1047 (s). Anal. Calc. for C₂₆H₂₃N₃O₂: C 76.26, H 5.66, N 10.26%; Found: C 76.03, H 5.14, N 11.47 %.

2.2.2 Preparation of L4

4-(4-(Bis(4-ethoxyphenyl)amino)styryl)benzaldehyde (0.46 g, 1 mmol), malononitrile (0.073 g, 1.1 mmol) and drops of piperidine were dissolved in ethanol (30 mL), refluxed overnight and monitored by TLC to ensure complete reac-

tion. Then, the mixture was cooled to room temperature, poured into CH₂Cl₂ (300 mL), washed with water (50 mL × 4) and dried over MgSO₄. The solvent was evaporated, and the residue was purified by column chromatography of silica gel with ethyl acetate/petroleum ether mixture (1:50 ν/ν) as the eluent. **L4** was obtained as a yellow solid in 60% yield. ¹H NMR (400 MHz, *d*₆-DMSO) δ (ppm): 7.95 (s, 1H), 7.55 (d, 2H, *J* = 8.0 Hz), 7.40(d, 2H, *J* = 8.8 Hz), 7.34(d, 2H, *J* = 7.2 Hz), 7.28(s, 2H), 7.24 (d, 2H, *J* = 8.4 Hz), 7.17 (d, 2H, *J* = 17.2 Hz), 7.12 (d, 1H, *J* = 16.0 Hz), 6.97 (1H), 6.74 (d, 2H, *J* = 7.6 Hz), 6.57 (d, 1H, *J* = 8.0 Hz), 6.48 (1H), 3.97(m, 4H), 1.34(t, 6H). FT-IR (KBr cm⁻¹): 2982, 2922, 2861 (m), 2216 (C=N, m), 1621 (m), 1561 (s), 1500 (s), 1248 (s), 1188 (s). Anal. Calc. for C₃₄H₂₉N₃O₂: C 79.82, H 5.71, N 8.21%; Found: C 79.50, H 5.43, N 7.94%.



Scheme 2 The synthetic routes for L1–L4. L1 (Ar = 4-(diphenylamino) benzaldehyde), L2 (Ar = -(4-(diphenylamino)-styryl)benzaldehyde), L3 (Ar = 4-(bis(4-ethoxyphenyl)amino)benzaldehyde), L4 (Ar = 4-(4-(bis (4-ethoxyphenyl)-amino)styryl)benzaldehyde).

3 Results and discussion

3.1 Synthesis

Schemes 1–2 show the chemical structures of L1–L4 and the respective preparation processes in this study. The organic compounds are obtained through the Knoevenagel condensation of malononitrile and the corresponding aldehydes. The foregoing spectroscopic data are in line with the designed structures.

3.2 Thermogravimetric analysis of L1–L4

Thermal stability is an important property of a designed organic compound. The results of the TG measurements are listed in Figure 1. L1–L4 exhibit high thermal stability and the quickest decomposition temperature ($T_{decomp.}$) of L1–L4 ranges from 318 °C to 410 °C.

In order to improve the thermal stability of D- π -A type compounds, there are many routes to adjust the structure. In this work, it is observed that the difference of an electron-donating unit and the systematically extended π -conjugated length affects the thermal stability of D- π -A type compounds. L1 losses its weight from 274 °C to 326 °C



Figure 1 TG curves of L1–L4. The inserts are DTG curves.

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($T_{\text{decomp.}}$ is 318 °C). Compared to the thermal stability of L1, incorporation of either extended π -conjugated length or ethoxyl unit notably increases the thermal stability of L2–L4. L2 losses its weight from 318 °C to 405 °C ($T_{\text{decomp.}}$ = 381 °C). L3 losses its weight from 278 °C to 355 °C ($T_{\text{decomp.}}$ = 347 °C), and L4 losses its weight from 362 °C to 496 °C ($T_{\text{decomp.}}$ = 410 °C).

3.3 Linear absorption and single-photon excited fluorescence (SPEF)

In this study, an important goal beyond synthesis and the thermal property is to investigate the effect of the π -conjugated spacer length and the ethoxyl unit on the optical properties. The photophysical properties of **L1–L4** in five different solvents (benzene, CH₂Cl₂, EtAc, THF, and DMF) at the concentration of 1.0×10^{-6} mol/L are collected in Table 1, including single-photon absorption and fluorescence, the corresponding fluorescence decay lifetime and quantum yields.

3.3.1 Linear absorption

Linear absorption spectra of L1–L4 in five different solvents are shown in Figure 2. As can be seen from Table 1 and Figure 2, the absorption spectra of L1 and L3 exhibit

one peak, which centers at about 420–440 nm in the selected solvents for L1 and 430–440 nm for L3, which corresponds to the π - π * transition of the main chain. The absorption spectra of L2 and L4 show two absorption maxima ($\lambda_{abs-max}$) between 250 nm and 450 nm, which are located at 294–312 nm, 394–407 nm for L2, and 283–294 nm, 390–400 nm for L4 in the five selected solvents, respectively. The longer wavelength at about 400 nm of L2 and L4 corresponds to the π - π * transition of the whole structure, while the shorter wavelength at about 300 nm is mainly associated with the π - π * transition of the triphenylamine moiety [16, 17]. The linear absorption properties of L1–L4 are further studied by TD-DFT calculation, which results in similar conclusion.

The $\lambda_{abs-max}$ of **L1–L4** is bathochromically shifted with the increasing polarity of the solvent. $\lambda_{abs-max}$ of **L1** is shifted by 12 nm from 428 nm in benzene to 440 nm in DMF, while that of **L2** is shifted by 13 nm from 394 nm in benzene to 407 nm in DMF, that of **L3** is shifted by 10 nm (431 nm in benzene and 441 nm in DMF), and that of **L4** is shifted by 10 nm (390 nm in benzene and 400 nm in DMF). This bathochromic shift reflects electron donating ability.

The results revealed that changing the π -conjugated length and/or introducing the ethoxyl unit to the electron-donating group can influence the electron-donating ability

 Table 1
 Photophysical properties of L1–L4 in several of different polar solvents

Compounds	Solvents	Benzene	CH ₂ Cl ₂	EtAc	THF	DMF
LI	$\lambda_{abs-max}$ (nm)	428	431	433	439	440
	$\mathcal{E}_{max} \times 10^{-4 a}$	0.98	3.33	3.08	2.80	2.10
	$\lambda_{\text{em-max}}$ (nm)	514	545	572	577	585
	$\phi^{\mathrm{b})}$	0.06	0.009	0.01	0.01	0.02
	$\Delta v (\mathrm{cm}^{-1})^{\mathrm{c}}$	3909	4853	5612	5448	5633
	τ (ns) d	2.39	3.38	2.03	3.70	2.19
	$\chi^{e)}$	1.23	0.98	0.86	1.20	0.97
L2	$\lambda_{abs-max}$ (nm)	294 394	295 395	303 399	308 406	312 407
	$\mathcal{E}_{max} \times 10^{-4 a}$	3.29	5.32	3.47	4.18	3.96
	$\lambda_{\text{em-max}}$ (nm)	488	524	531	550	560
	$\phi^{\mathrm{b})}$	0.19	0.10	0.12	0.078	0.04
	$\Delta v (\text{cm}^{-1})^{\text{c}}$	4953	6232	6230	6449	6713
	τ (ns) ^{d)}	2.10	2.69	2.32	2.35	2.43
	$\chi^{e)}$	1.06	1.09	1.32	0.94	1.08
L3	$\lambda_{abs-max}$ (nm)	431	432	434	437	441
	$\mathcal{E}_{max} \times 10^{-4 a}$	1.40	1.61	1.57	2.53	1.06
	$\lambda_{\text{em-max}}$ (nm)	509	520	519	523	533
	$\phi^{\mathrm{b})}$	0.14	0.10	0.09	0.11	0.11
	$\Delta v (\text{cm}^{-1})^{\text{c}}$	3609	3917	3774	3763	3914
	τ (ns) ^{d)}	2.86	1.42	2.43	2.41	0.234
	$\chi^{e)}$	1.21	0.97	1.02	0.92	1.05
L4	$\lambda_{abs-max}$ (nm)	283 390	289 393	294 397	288 399	290 400
	$\mathcal{E}_{max} \times 10^{-4 a}$	0.53	0.67	0.54	0.63	0.63
	$\lambda_{\text{em-max}}$ (nm)	509	527	531	552	559
	$\phi^{\mathrm{b})}$	0.23	0.11	0.05	0.026	0.023
	$\Delta v (\mathrm{cm}^{-1})^{\mathrm{c}}$	5995	6470	6356	6947	7174
	τ (ns) ^{d)}	3.63	2.50	1.63	1.58	3.07
	$\chi^{e_{i}}$	1.18	1.13	1.09	1.12	1.02

a) One-photon absorption coefficients (ε is in unit of dm³ mol⁻¹ cm⁻¹); b) quantum yields determined by using fluorescein as standard; c) Stokes' shift; d) FL lifetime; e) goodness of fit.



Figure 2 Linear absorption spectra of L1–L4 in five different solvents.

of the triphrnylamine group. Furthermore, the different electron-donating ability may influence the bandgap of the intramolecular charge-transfer material, which will result in different linear absorption properties. Similar phenomenon is expected to appear in single-photon excited fluorescence.

3.3.2 Single-photon excited fluorescence (SPEF)

The SPEF spectra (Figure 3) and the corresponding FL lifetime (Figure 4) have been measured under the same conditions as the linear absorption spectra. As shown in Figure 3 and Table 1, the SPEF spectra of L1-L4 display positive solvatochromism (red-shift with increasing solvent polarity) in their emission spectra. Moreover, the fluorescence intensity decreases with the increasing solvent polarity. For example, the maximum emission wavelength of L1 centers at about 514 nm in benzene (I = 1262 a.u.), while in a higher polar solvent DMF, the peak locates at 583 nm (I = 852a.u.), which is red-shifted by 69 nm and one third decrease of intensity due to different molecular environment. The SPEF spectra of L2, L3 and L4 all exhibit the same trend. The peak of L2 red shifts by 72 nm from 495 nm in benzene (I = 10035 a.u.) to 567 nm in DMF (I = 1981 a.u.). The peak of L3 red shifts by 34 nm (509 nm in benzene with I = 5313a.u. and 533 nm in DMF with I = 2315 a.u.) and that of L4 is 60 nm (509 nm in benzene with I = 93082 a.u., 559 nm in DMF with I = 666 a.u.). Large values of the Stokes' shift are observed for L1–L4 in the selected solvents due to strong solvent-solute dipole-dipole interactions, which exhibit large orientational polarizability and dipole moment.

As L1–L4 contain electron-donating group (triphenylamine) and electron-withdrawing group (dicyano), charge separation in the fluorophore is their most significant character, which results in dipole moment in the ground state. Meanwhile, in the excited state, the degree of charge separation increases, and a larger dipole moment appears than that in the ground state [18]. The charge separation will be even larger with the increasing of solvent polarity. Thus, the emission spectra of the four compounds exhibit remarkable solvent polarity sensitivity.

Comparing the bathochromically shifted emission wavelength between L1 and L2 (69 nm for L1 and 72 nm for L2, respectively), L3 and L4 (34 nm for L3 and 60 nm for L4, respectively), one can see that extending π -linkage length results in increasing positive solvatochromism. The result is consistent with the observations of UV-Vis absorption experiments.

Comparing to the SPEF spectra of L1, L2–L4 showed blue-shifted emission wavelength no matter when extending the π -linkage unit or introducing the ethoxyl unit to the triphenylamine group. This may be resulted from the easy-

L2

0

0

450

450

L4

500

500

550

550

Wavelength (nm)

Wavelength (nm)

600

Benznen

CH,CI,

EtAc

THE

DMF

600

650



Figure 3 The single-photon excited fluorescence spectra of L1-L4.



As can be seen in Table 1, the fluorescence quantum yields of L1-L4 change a lot with different solvents. The emission quantum yields show a trend of reduction along with the red shift of SPEF. For example, the fluorescence quantum yield of L1 in benzene is 0.06, while it is reduced to 0.01 in EtAc and THF. The result indicates that in polar solvents, the intermolecular interactions between the dye molecules and the solvent molecules in the excited state are stronger than that in the non-polar solvents, which induces a further increase of the effect of energy- and/or chargetransfer processes between the excited and the ground state of the dye molecules. Thus, a decrease of energy in the excited state is expected, accompanied by a red shift of SPEF and decrease of fluorescence quantum yield.

In this study, higher Φ values are obtained in non-polar solvents with the highest Φ values being observed in C₆H₆. Therefore, the results in C₆H₆ are chosen to be discussed as an example. The fluorescence quantum yields of L2 are



3.3.3 Time-resolved measurements

The time-resolved PL decays of L1-L4 are measured using a time-correlated single-photon counting (TCSPC) technique. SiO₂ nanocrystals in H₂O sample is used as an IRF reference for the life-times reconvolution. During the measurements, compounds are excited with the optimal excitation wavelength (λ_{ex-max}) in order to obtain the largest relative fluorescence intensity. The data shown in the study is examined at the λ_{em-max} of L1-L4 respectively. The fluorescence decay profiles of L1-L4 in five different solvents are shown in Figure 4. The results in THF solutions will be discussed in detail as an example. The fluorescence decay lifetimes and its amplitude in THF are summarized in Table 2. The fluorescence of L1, L3 in THF is found to decay with two components, while L2, L4 in THF is found to de-

Benznen

CH,CI,

EtAc

THF

DMF

650

700

700



Figure 4 Time-domain fluorescence intensity decay of L1-L4.

Table 2 Fluorescence decay lifetime (τ) and amplitude (A) of L1–L4 in THF solution

Compounds	$\lambda_{\rm em} ({\rm nm})$	τ1 (ns)	A1 (%)	<i>t</i> 2 (ns)	A2 (%)	<i>τ</i> 3 (ns)	A3 (%)	$\overline{\tau}$ (ns)	χ
L1	577	0.80	24.7	2.43	75.3	-	-	2.03	0.86
L2	550	1.21	6	2.26	91	4.20	3	2.26	0.98
L3	523	1.48	10.5	2.52	89.5	-	-	2.41	0.92
L4	552	0.89	64	3.76	28	12.50	7	2.50	1.13

cay with three components. There are two kinds of mechanisms to explain the multi-exponential of FL lifetime. One is that there exist more than one component in the excited state and each component has its inherent FL lifetime. The other is that the fluorophore exists as a dimer and/or trimer in the solution. As for the latter mechanism, there will be a longer wavelength emission in the SPEF [20–22]. However, the experimental result shows only one peak for L1–L4, which rules out the second mechanism. The result reveals that there are more than one component in the excited state of L1–L4. As for L1 and L3, there exist two kinds of excited state, which is in accordance with the two excitation bands (see Supporting Information Figure S2). On the other hand, there exist three kinds of excited state of L2 and L4. For detail, in the THF solution of L1 at 577 nm emission, a short component has a decay lifetime of 0.80 ns (the corresponding amplitude is 24.7%), and the following component has 2.43 ns (75.3%). With extending π -conjugated length to L2, the fluorescence decay lifetime and the corresponding amplitude of a short component are 1.21 ns and 6%, respectively. The decay lifetime of the following component is 2.26 ns with amplitude being 91%. It is worth noting that there exists the third component with the fluorescence decay lifetime and the corresponding amplitude being 4.20 ns and 3%, respectively. The similar trend is also observed between L3 and L4. The results reveal that the extended π -conjugated length leads to additional excited state. However, the emission band of L1–L4 shows only

one peak. In the case of this point, the intense of other bands should overlap the existing band or they appear as shoulder on the spectrum.

The average fluorescence decay lifetime of L3 at 523 nm emission is 2.41 ns, which is longer than that of L1 (2.03 ns at 577 nm emission band). The same trend also appears between L2 and L4 ($\overline{\tau} = 2.26$ ns for L2 at 550 nm emission band and 2.50 ns for L4 at 552 nm), i.e, introducing the ethoxyl unit to the electron-donating group seems to provide a more stable environment for the excited state.

3.4 Theoretical calculations

As is well known that electronic excitation from the HOMO to the LUMO produces the first singlet excited state. Thus, molecular orbital calculations of TD-DFT at the B3LYP level basis set (Gaussian 03 [23]) are performed on compounds L1–L4 to study their electronic structures. The orbital features presented in Table 3 might provide insights to understand the corresponding optical properties of the com-

pounds. In the HOMO, the electrons are primarily concentrated on the nitrogen atom of the triphenylamine and its adjacent benzene ring. In the LUMO, the electrons are mainly concentrated on cyano group and its adjacent benzene ring. Obviously, the electron transition from the HOMO to the LUMO is accompanied by intramolecular charge transfer from the central triphenylamine moiety to the peripheric cyano unit. The calculated HOMO-LUMO gap is 3.11 eV for L1, 2.40 eV for L2, 2.80 eV for L3 and 2.21 eV for L4.

Introduction of the ethoxyl unit to the triphrnylamine group leads to little energy changes of the LUMO orbits (-2.50 eV for L1 and -2.48 eV for L3, for example), and significant energy changes of the HOMO orbits (-5.61 eV for L1 and -5.28 eV for L3). Thus, the HOMO-LUMO gap decreases from L1 (3.11 eV) to L3 (2.80 eV). The same trend is also observed for L2 and L4. These results show that the strong electron-donating unit (ethoxyl unit) may raise the HOMO level and lead to smaller gap [12]. The extended π -conjugated length can both raise the HOMO

Table 3 Frontier orbital and the corresponding energy of L1-L4 in the gas phase



level and lower the LUMO level, which will lead to an even smaller HOMO-LUMO gap (comparing L1 to L2, L3 to L4).

The theoretical spectral characteristics, detailed information is shown in the Supporting Information Table S1, show one main transition for L1 (λ_{abs} = 421 nm) and L3 (λ_{abs} = 437 nm), which is just from the HOMO orbit to the LUMO. When extending the π -conjugated length of L2 and L4, the theoretical spectra show two main optical transitions. One transition corresponds to the transition from the configuration HOMO-1 to LUMO with $\lambda_{abs} = 386$ nm (oscillator strength $f_{(HOMO-1)-LUMO}$ being 0.9789) for L2 and $\lambda_{abs} =$ 405 nm ($f_{(HOMO-1)-LUMO}$ being 0.9885) for L4, respectively. The other optical transition for L2 corresponds to the configuration HOMO to LUMO+3 with $\lambda_{abs} = 308$ nm and $f_{\text{HOMO-(LUMO+3)}}$ being 0.1336. While the other transition for L4 corresponds to the configuration HOMO to LUMO+4 with $\lambda_{abs} = 300$ nm and $f_{HOMO-(LUMO+4)}$ being 0.1733. The calculated results fit with the experimental data and the corresponding absorption bands are observable on the absorption spectra of L1-L4.

3.5 Two-photon absorption (TPA) and two-photon excited fluorescence (TPEF)

As shown in linear absorption spectra, there is no linear absorption in the wavelength range of 550-900 nm for **L1–L4**. It is inferred that there are no energy levels corresponding to one electron transition in this spectral range. Therefore, the two-photon excited fluorescence (TPEF) pathway is expected to appear if frequency up-converted fluorescence induced with a laser in this range appears [24]. The insets of Figure 5 show log-log plot of the excited fluorescence signal *vs*. excited light power. The linear dependence of the square of input laser power on the output fluorescence intensity (with a slope of 2.04, 2.03, 1.98 and 2.02 for **L1–L4** respectively) provides direct evidence for two-photon excited process.

The TPA cross-sections have been measured using the two-photon-induced fluorescence measurement technique [25]. The TPA cross sections (δ) are determined by comparing their two-photon excited fluorescence to that of fluorescening in the NaOH solution (aq, 0.1 mol/L) (pH = 11) [26, 27] according to the following equation [28]



Figure 5 TPF spectra of L1–L4 in DMF solution pumped by femtosecond laser pulses under different pumped powers at their maximum excitation wavelength, insert is the logarithmic plots of the output fluorescence $(I_{out}) vs$. the square of input laser power (I_{in}) .

$$\delta = \delta_{\rm ref} \frac{\Phi_{\rm ref}}{\Phi} \frac{C_{\rm ref}}{C} \frac{n_{\rm ref}}{n} \frac{F}{F_{\rm ref}}$$
(1)

In this equation, the subscripts ref refers to the reference molecule, which is fluorescein. δ is the TPA cross-section 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 equals to 38, which is from the literature [26, 27, 29].

Detailed experiments reveal that the peak position in the TPEF spectra of L1–L4 are independent of the excitation wavelengths from 680 to 900 nm, while the TPA cross sections change over this range. Thus, by tuning the pump wavelengths incrementally from 680 to 900 nm while keeping the input power fixed and then recording the TPEF intensity, the two-photon absorption spectra are obtained as shown in Figure 6. The best TPA wavelength is 720 nm for L1, 800 nm for L2, 780 nm for L3, and 800 nm for L4. The best excitation wavelength of L4 is essentially twice that of the linear absorption maximum (400 nm). For L1–L3, The best excitation wavelength is slightly shorter than twice that of the corresponding linear absorption maximum (440, 407 and 441 nm for L1, L2 and L3, respectively).

As shown in Figure 5, the emission maximum locates at 588 nm for L1, 586 nm for L2, 550 nm for L3 and 575 nm for L4, respectively. The TPEF peak position of L1 is very close to the peak fluorescence wavelength using SPEF, while the TPEF peak position of L2–L4 shows a red-shift when compared to that of SPEF (Figure 3 and Table 1). This can be explained by the effect of re-absorption. For single-photon induced emission measurements, dilute solutions $(1 \times 10^{-6} \text{ mol L}^{-1})$ were used, thus the re-absorption of SPEF within the samples is negligible. In the case of TPEF, concentrated solutions $(1 \times 10^{-3} \text{ mol L}^{-1})$ were used. The emission is from the surface layer as well as inside the solution sample. Thus, re-absorption of the shorter wavelength fluorescence by the concentrated sample can no longer be

neglected. As mentioned above, the molecules of L1 tend to self-assembly. Thus the aggregate effect may be the main influencing factor for L1, which can explain the phenomena that the TPEF peak position of L1 is very close to that of the SPEF. However, the re-absorption effect may be more important for L2–L4.

According to Eq. (1), the largest δ_{TPA} is 87 GM (1 GM = 10^{-50} cm⁴ s photon⁻¹) for L1 at 720 nm excitation, 3733 GM for L2 at 800 nm, 18 GM for L3 at 780 nm, and 144 GM for L4 at 800 nm, respectively. It is worthwhile noting that δ is strongly enhanced with the increasing π -linkage length. Comparing L2 to L1, the value offers a > 40-fold increase. Meanwhile, the ethoxyl unit also influences the optical property. Comparing L1 to L3, the value offers a ~ 5-fold increase, which confirms the effect of the ethoxyl unit on the charge recombination in the whole structure.

4 Conclusions

Systematic study on preparation, thermal stability, linear absorption, single- and two-photon excited fluorescence, and theoretical calculation on a series of ICT type triphenylamine derivatives allows us to derive significant structure-property relationships. The chromophores show high thermal stability, good single- and/or two-photon excited fluorescence behavior, and have potential applications as lighter-emitting materials. The extended π -conjugated length leads to additional fluorescent excited state. It can improve the fluorescence quantum yields and enhance TPEF spectra as well as the corresponding TPA cross sections. Introducing the ethoxyl unit to the triphenylamine group can improve the fluorescence quantum yields, provide a more stable environment for the excited state and balance the charge recombination in the whole structure. This study can provide some insights and strategies in designing and preparing organic optical materials with potential values.



Figure 6 Two-photon absorption cross sections of L1-L4 in DMF vs. excitation wavelengths of identical energy of 0.50 W.

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