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Two novel terpyridine-based chromophores with donor-acceptor structural model containing modified triphenylamine moiety: Synthesis, crystal structures and two-photon absorption properties

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Two novel terpyridine-based chromophores with D-A (D = donor, A = acceptor) structural model containing modified triphenylamine moiety (\mathbf{L}^1 and \mathbf{L}^2) have been conveniently synthesized *via* formylation and reduction in satisfactory yields, and fully characterized. The single crystals of them were obtained and determined by X-ray diffraction analysis. The relationships between structure and photophysical properties of the two chromophores were investigated both experimentally and theoretically. The measured maximum TPA cross-sections per molecular weight (δ_{max}/MW) of the chromophores are 0.63 GM/(g mol) (\mathbf{L}^1) and 0.72 GM/(g mol) (\mathbf{L}^2), respectively, in DMF as a high polar solvent. The results indicate that the value of δ_{max}/MW could be well tuned by the intramolecular charge transfer (ICT), which could be realized by introducing additional electron-donor/acceptor groups.

terpyridine derivatives, photophysical properties, structure-property relationships, TD-DFT calculation, two-photon-excited fluorescence

1 Introduction

The two-photon absorption (TPA) process was theoretically predicted by Maria Göppert-Mayer [1] in the 1931, and first experimentally proved after the appearance of laser sources in 1961 [2]. Since then, its practical significance has been recognized by pioneering efforts. Significant advances have been made in a great variety of potential applications in the areas of three-dimensional (3D) optical storage [3–6], multiphoton fluorescence imaging [7–13], 3D micro-fabrication

[7, 14, 15], photodynamic therapy [16–18], two-photon up-conversion lasing [19, 20] and optical power limiting [21–23].

Along with the aforementioned promising applications, efforts are also focused on designing and synthesizing new materials with striking TPA effect and large TPA cross-section (δ_{TPA}) values. Up to now, several strategies [24–30] have successfully been employed to achieve the aim, such as enhancing the amount of branches, expanding the effective length of conjugation, improving ICT efficiency, changing the strength of the donor and acceptor, and/or increasing the planarity of the π center and so on. Although

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most organic molecules with strong TPA effect have been synthesized, the reaction routes may be long, complex, and inevitably the target compounds may be obtained in low yields. Moreover, there exists another important problem concerning comparison of nonlinear absorption efficiency among disparate types of chromophores with different molecular weight, molecular volume, financial cost-scaling and the number of effective electronic distribution for the benefit of TPA effect, *etc* [31–33]. Therefore, it is challenging for us to develop materials with large δ_{TPA} which are based on a relatively reasonable approach to scale NLO data, in addition to facile synthesis and high yields.

Based on the aforementioned considerations, we designed two novel D-A structural chromophores with triphenylamine moiety as the electron donor (D) and 2,2':6',2"-terpyridine, as the acceptor (A). The building blocks of triphenylamine and terpyridine always employed to construct TPA chromophores [34, 35]. Apart from that, we have other important reasons for the selection of the two chromophores: (1) it is apparent that the route used is more simpler, and higher yield can be achieved at almost every step; (2) the properties of the chromophores (L^1 and L^2 presented in Figure 1) TPA will be relatively accurate compared by TPA cross-section per molecular weight (δ_{max}/MW) owing to their almost approximate molecular volume and production costs; (3) the subtle structural modifications only appear at the terminal of the triphenylamine moiety in the molecular skeleton, which will lead to increase of the TPA across section values.

The two target chromophores were synthesized *via* formylation and aldehyde group reduction starting from 4'-(4-(diphenylamino)phenyl)-2,2':6',2"-terpyridine, as illustrated in Scheme 1. Their photophysical properties, such as linear absorption, single- and two-photon excited fluorescence in various solvents, were systematically studied. Furthermore, the connections between the structure and properties of the chromophores were investigated both experi-



Figure 1 Molecules of dye L^1 and dye L^2 .

mentally and theoretically.

2 Experimental

2.1 Materials and apparatus

All chemicals were purchased as analytical grade and used without further purification. The solvents were purified by conventional methods. Mass spectrum was determined with a Micro-mass GCT-MS (EI source). IR spectra were recorded on NEXUS 870 (Nicolet) spectrophotometer in the 4000–400 cm⁻¹ region with samples prepared as KBr pellets. ¹H- and ¹³C-NMR spectra were obtained on a Bruker Avance 400 MHz spectrometer at 25 °C (TMS as internal standard in NMR).

X-ray diffraction data of single crystals were collected on a CCD diffractometer. The determination of unit cell parameters and data collection were performed with Mo- K_{α} radiation ($\lambda = 0.71073$ Å). Unit cell dimensions were obtained with least-squares refinements, and all structures were solved by direct methods using SHELXS-97 [36]. The other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full-matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2 . The hydrogen atoms were added theoretically riding on the concerned atoms.

UV-vis absorption spectra were recorded on a UV-265 spectrophotometer. Fluorescence measurements were performed at room temperature using a Hitachi F-7000 fluorescence spectrophotometer. The fluorescence quantum yields (Φ) were determined against the quinine sulfate standard. TPEF spectra were measured using femtosecond laser pulse and Ti: sapphire system (680–1080 nm, 80 MHz, 140 fs, Chameleon II) as the light source. With excitation at the optimal excitation wavelength (λ_{ex-max}), time-resolved decay curves were performed on fluotime200 (Pico Quant) using a time-correlated single-photon counting (TCSPC) technique. SiO₂ nanocrystals in H₂O sample were used as an IRF reference for the lifetime reconvolution.

2.2 Synthesis

2.2.1 4'-(4-(4,4-Diphenylamino)-phenyl-2,2':6',2"-terpyridine (L^{0})

 L^0 was synthesized according to a previously reported



Scheme 1 Synthetic routes for two dyes L^1-L^2 .

method [37].

2.2.2 4'-(4-(4-phenyl-4'-aldehydicphenyl) amino) phenyl-2,2':6',2"-terpyridine (L^1)

At ice salt bath temperature, POCl₃ (2.1 g, 13.7 mmol) was added dropwise to a three-necked flask containing DMF (1.0 g, 13.7 mmol). After the frozen salt appeared, L^0 (0.5 g, 1 mmol) dissolved in CHCl₃ (50 mL) was added, and then refluxed for 24 h. After cooled to room temperature, the mixture was poured into a large amount of ice water and adjusted to pH = 8 using NaOH. After extracting with CH₂Cl₂, the mixture was dried over anhydrous Na₂SO₄ and evaporated to yield a yellow solid. The solid was purified by silica gel chromatography column using petroleum/ethyl acetate (5/1 V/V) as the eluent with 76% yield (0.40 g). ¹H-NMR (400 MHz, CDCl₃, TMS), δ (ppm): 9.88 (s, 1H), 8.99-8.87 (m, 6H), 8.15-8.05 (m, 4H), 7.77-7.75 (d, 2H), 7.58-7.58 (d, 2H), 7.33-7.31 (d, 2H), 7.24-7.22 (m, 3H), 7.16-7.14 (d, 2H). ¹³C-NMR (100 MHz, CDCl₃, TMS), δ (ppm): 190.48, 156.13, 155.91, 152.97, 149.44, 149.06, 147.12, 146.01, 136.99, 134.61, 131.34, 129.87, 129.76, 128.65, 126.44, 125.76, 125.40, 123.90, 121.40, 120.36, 118.61. MS, *m/z* (%): 504.20 (100).

2.2.3 4'-(4-(4-phenyl-4'-hydroxymethyl phenyl) amino) phenyl-2,2':6',2"-terpyridine (L^2)

Chromophore L^1 (0.5 g, 1.0 mmol) was dissolved in 150 mL EtOH. Then 0.19 g (5.0 mmol) NaBH₄ was slowly added as a solid. The reaction flask was placed in an oil bath at 80°C. The reaction was monitored by TLC. After the completion of the reaction, the solvent was removed under reduced pressure. The solid was recrystallized from EtOH. After filtration and drying under vacuum, L^2 was obtained as a slightly yellow solid. Yield 91.6% (0.46 g). ¹H-NMR (400 MHz, CDCl₃, TMS), δ (ppm): 8.74-8.67 (m, 4H), 8.69-8.67 (d, 2H), 7.92-7.88 (t, 2H), 7.82-7.80 (d, 2H), 7.38-7.35 (m, 2H), 7.32-7.29 (m, 4H), 7.20-7.15 (m, 6H), 5.29 (s, 1H), 4.67 (s, 2H). ¹³C-NMR (100 MHz, CDCl₃, TMS), δ (ppm): 156.23, 155.70,149.76, 148.97, 148.71, 147.29, 146.93, 137.02, 135.80, 131.85, 129.41, 128.37, 128.18, 124.85, 124.71, 123.81, 123.50, 123.16, 121.43, 118.39, 65.05. MS, *m*/*z* (%): 506.40 (100).

3 Results and discussion

3.1 Synthesis

The synthetic route toward the D-A target ligands (L^1 and L^2) is depicted in Scheme 1. L^0 was obtained by the Ullmann condensation according to the previously reported method. Through the Vilsmeier-Haack reaction, L^1 was synthesized with the 76% yield. Owing to the influence of the electron withdrawal and space baffle existing in the chromophore L^0 , it is necessary to increase the reactant ratio for L^0 , DMF and POCl₃, and to prolong the reaction time

for the desired yield. Using NaBH₄ as the reductive, the final chromophore L^2 was almost quantitatively achieved by the reduction of L^1 . In conclusion, the two novel dyes could be conveniently synthesized in high yields.

3.2 Crystal structures

The crystallographic data, selected bond lengths and angles for L^0 , L^1 and L^2 are summarized in Table 1 and Table S1. The crystal structures of L^1 and L^2 are shown in Figures 2 and 3, respectively. To illustrate the conformation of them, parameters P1-P6 are presented in Table 2.

3.2.1 Similarities of their structures

It can be seen that the terpyridyl group as an acceptor in L^1 and L^2 is coplanar like that of L^0 , in which the dihedral angles are given in Table 2. Another same structural unit in L^0 , L^1 and L^2 is the triphenylamine as a donor. Due to the sp²

Table 1 Crystal data collection and structure refinement of L^0 , L^1 and L^2

| Compound | L ^{0 a)} | L^1 | L^2 | |
|-------------------------------|-------------------|--------------------|--|--|
| Chemical formula | $C_{32}H_{24}N_4$ | $C_{34}H_{24}N_4O$ | $\mathrm{C}_{34}\mathrm{H}_{26}\mathrm{N}_{4}\mathrm{O}$ | |
| Formula weight | 476.57 | 504.57 | 506.60 | |
| Crystal system | Triclinic | Monoclinic | Orthorhombic | |
| Space group | $P\overline{1}$ | $P2_1/c$ | $P2_{1}2_{1}2_{1}$ | |
| <i>a</i> (Å) | 9.298(5) | 14.493(5) | 14.899(5) | |
| $b(\text{\AA})$ | 11.366(5) | 10.074(5) | 26.354(5) | |
| $c(\text{\AA})$ | 12.783(5) | 18.050(5) | 7.292(5) | |
| α (°) | 107.334(5) | 90.000(5) | 90.000(5) | |
| β (°) | 98.911(5) | 101.068(5) | 90.000(5) | |
| $\gamma(^{\circ})$ | 98.521(5) | 90.000(5) | 90.000(5) | |
| $V(Å^3)$ | 1246.7(10) | 2586.30(17) | 2863(2) | |
| Ζ | 2 | 4 | 4 | |
| $R_1, wR_2(I \ge 2\sigma(I))$ | 0.0428, 0.0980 | 0.0391, 0.0925 | 0.0481, 0.0943 | |
| R_1 , $wR_2(all data)$ | 0.0676, 0.1159 | 0.0601, 0.1059 | 0.0861, 0.1123 | |
| Goodness-of-fit on F^2 | 0.970 | 0.994 | 0.983 | |

a) Crystal data cited from the Ref. [30].



Figure 2 Crystal structure of L^1 (hydrogen atoms are omitted for clarity).



Figure 3 Crystal structure of L^2 (hydrogen atoms are omitted for clarity).

Table 2 Conformational parameters for L^0 , L^1 and L^{2a}

| Compound | Γ_0 | L^1 | L^2 |
|------------------|------------|--------|--------|
| P _{6,0} | 64.82° | 31.00° | 53.59° |
| $P_{6,1}$ | 49.36° | 50.17° | 26.43° |
| P _{6,2} | 29.47° | 40.02° | 35.23° |
| P _{2,3} | 32.50° | 36.74° | 25.91° |
| P _{3,4} | 4.16° | 6.44° | 4.95° |
| P _{3,5} | 6.79° | 11.48° | 5.38° |

a) P_{6,0} represens the dihedral angles between P₆ and P₀, and so on.

hybrid of the central nitrogen atom of triphenylamine moiety, the nitrogen and its three adjacent carbon atoms are approximately coplanar (named as the P6 plane), with the sum of the three C–N–C angles (360.0°) and almost the same C–N bond length. However, the three phenyl ring planes are arranged in a propeller-like fashion owing to space repulsion among the phenyl rings, thus avoiding molecule aggregation, and resulting in a highly soluble amorphousness.

3.2.2 Differences between the crystal structures of L^{0-2}

Compared with the crystal structures between L^0 and L^1 , there is an aldehyde group (–CHO), a medium electron withdrawing group (EWG), attached to the triphenylamine moiety in L^1 , resulting in their structural changes, presented in Tables 1, 2 and S1. The differences between them are concluded as follows. (1) They belong to two crystal systems, triclinic and monoclinic, and two space groups, $P_{\overline{1}}$ and $P_{2_1/c}$. (2) The –CHO unit is well conjugated with the phenyl ring (PO) with the bond length of C(31)–C(34): 1.47 Å, which is between the normal C=C double bond (1.34 Å) and C–C single bond (1.54 Å) showing that there is a partially delocalized π -electron system in L^1 molecule. Apart from that, the dihedral angle of $P_{6,0}$ decreases from 64.82° (**L**⁰) to 31.00° (**L**¹).

Compared with L^1 , a hydroxymethyl substituent (-CH₂OH), a weaker electron-donor group (EDG), is introduced to the triphenylamine moiety in L^2 . Interestingly, the subtle modification also leads to several differences as follows. (1) It is found that the crystal system and space group of L^2 are orthorhombic and $P_{2,1}_{2,1}_{2,1}$, respectively. (2) The bond length of C(31)–C(34) (1.50 Å) is slightly longer than that of C(31)–C(34) in L^1 , which may result from the sp³ hybrid of C atom in the –CH₂OH unit. (3) The dihedral angle of P_{6,0} increases to 53.59°, due to the plane of P₀' without well delocalization with the adjacent N atom, which is 31.00° in L^1 . (4) The bond length of N(4)–C(28) in L^1 is shorter than that in L^2 .

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

3.3.1 Linear absorption properties

The photophysical data of the three chromophores (\mathbf{L}^{0} , \mathbf{L}^{1} and \mathbf{L}^{2}) are summarized in Table 3. The linear absorption of the chromophores in seven different solvents with the concentration of 1.0×10^{-5} mol \mathbf{L}^{-1} is shown in Figures 4 and S1, respectively.

From those absorption spectra, it is apparent that L^0 and L^2 exhibit dual bands in the 270–450 nm range, while L^1 displays three bands in the same region. The longer wavelength band at about 350-370 nm is attributed to ICT transition or $\pi \rightarrow \pi^*$ transition of the whole molecule for the chromophores L^0 , L^1 and L^2 , while the shorter wavelength band near 290 nm is attributed to the absorption of the triphenylamine moiety. Additionally, a shoulder band of L^1 also appeared at about 335 nm, which is consistent with the crystal structural feature above. This band is assigned to the π orbital electron of the aldehyde group transition to the π^* orbit of the whole molecule because the values of the maximum molar extinction coefficient (ε_{max}) are all more than 2.0×10^4 mol⁻¹ L cm⁻¹ in different selected solvents. As shown in Figures 4 and S1, little solvatochromism was observed by increasing the solvent polarity, indicating that the little difference in dipoles between the ground and excited state of the chromophores was observed in spite of peripheral solvents' polarity. Another feature is that the maximum absorption bands of \mathbf{L}^1 and \mathbf{L}^2 are red-shifted by 12 nm and 3 nm, respectively, relative to that of L^0 at 356 nm in ethyl acetate solvent. The results reveal that introducing different units to the triphenylamine group can influence the electron-donating ability of it. Furthermore, the different electron-donating ability may influence the bandgap of the intramolecular charge-transfer of the chromophores as well, which will result in different linear absorption properties. These findings can also be supported by theory calculations as follows.

Table 3 Single-photon-related photophysical properties of L^0 , L^1 and L^2 in several different solvents

| Compds | Solvents | $\lambda_{\max}^{a} (\mathcal{E}_{\max}^{b)})$ | $\lambda_{\max}^{c)}$ | $\Delta v^{(d)}$ | ${\it I}\!$ | τ (ns) ^{f)} | $k_{\rm r}^{ m g)}$ | $k_{\rm nr}^{\rm h)}$ |
|------------------------|----------------------------------|--|-----------------------|------------------|---|---------------------------|---------------------|-----------------------|
| Γ_0 | C_6H_6 | 288(3.74) 360(2.75) | 430 | 4522 | 0.65 | 1.98 | 3.28 | 1.77 |
| | CH_2Cl_2 | 287(3.92) 358(2.98) | 466 | 6474 | 0.48 | 2.82 | 1.70 | 1.83 |
| | CH ₃ COOEt | 286(3.75) 356(2.86) | 447 | 5719 | 0.60 | 3.23 | 1.86 | 1.24 |
| | THF | 288(3.64) 357(2.65) | 448 | 5711 | 0.70 | 2.70 | 2.59 | 1.11 |
| | CH ₃ CN | 286(4.02) 351(3.03) | 491 | 7882 | 0.29 | 4.83 | 0.61 | 1.46 |
| | EtOH | 285(3.72) 358(2.73) | 499 | 7432 | 0.17 | 2.59 | 0.65 | 3.21 |
| | DMF | 287(3.33) 359(2.59) | 485 | 7006 | 0.46 | 5.19 | 0.90 | 1.03 |
| \mathbf{L}^{1} | C_6H_6 | 278(2.91) 335(2.62) 372(3.50) | 452 | 4758 | 0.33 | 2.25 | 1.46 | 2.98 |
| | CH ₂ Cl ₂ | 282(2.85) 332(2.66) 376(2.93) | 507 | 6872 | 0.15 | 3.04 | 0.48 | 2.81 |
| CH ₃ THF | CH ₃ COOEt | 280(2.88) 338(2.92) 368(3.66) | 466 | 5715 | 0.26 | 3.84 | 0.68 | 1.92 |
| | THF | 278(2.93) 338(2.80) 370(3.66) | 464 | 5475 | 0.31 | 2.30 | 1.33 | 3.02 |
| | CH ₃ CN | 280(2.91) 335(2.70) 371(3.59) | 514 | 7499 | 0.03 | 2.92 | 0.11 | 3.31 |
| EtOH DMF | 284(2.81) 332(2.46) 370(3.59) | 496 | 6866 | 0.01 | 0.15 | 0.33 | 66.34 | |
| | DMF | 277(2.92) 338(2.64) 372(3.41) | 496 | 6720 | 0.12 | 3.38 | 0.36 | 2.60 |
| \mathbf{L}^2 | C ₆ H ₆ | 292(2.69) 362(2.07) | 438 | 4793 | 0.95 | 2.16 | 4.40 | 0.23 |
| | CH_2Cl_2 | 293(2.84) 361(2.17) | 470 | 6424 | 0.58 | 2.97 | 1.97 | 1.40 |
| | CH ₃ COOEt | 291(3.37) 359(2.69) | 456 | 5618 | 0.52 | 3.49 | 1.50 | 1.36 |
| | THF | 290(2.74) 360(2.09) | 457 | 5896 | 0.72 | 2.93 | 2.44 | 0.97 |
| | CH ₃ CN | 288(2.73) 358(2.16) | 499 | 7432 | 0.20 | 5.09 | 0.40 | 1.56 |
| | EtOH | 289(2.96) 362(2.20) | 506 | 7785 | 0.13 | 2.16 | 0.58 | 4.05 |
| | DMF | 292(2.69) 364(2.04) | 496 | 7311 | 0.44 | 5.61 | 0.78 | 1.00 |

a) Peak position of the largest absorption band in nm $(1.0 \times 10^{-5} \text{ mol } \text{L}^{-1})$; b) maximum molar absorbance in $10^4 \text{ mol}^{-1} \text{ L cm}^{-1}$; c) peak position of SPEF, exited at the absorption maximum; d) stokes shift in cm⁻¹; e) quantum yields determined by using quinine sulfate as standard; f) the fitted fluorescence lifetime; g) the rate constant of a radiative process $(1.0 \times 10^8 \text{ s}^{-1})$; h) the cumulative rate constant of a non-radiative process $(1.0 \times 10^8 \text{ s}^{-1})$.



Figure 4 Linear absorption and SPEF spectra of L^0 , L^1 and L^2 in ethyl acetate with a concentration of 1.0×10^{-5} mol L⁻¹.

3.3.2 TD-DFT computational studies

It is well known that electronic excitation from the HOMO to the LUMO produces the first singlet excited state. Thus, TD-DFT computational studies at the B3LYP level basis set were also carried out for L^1 and L^2 using the G03 software [38]. Figure 5 gives straight-forward representations of the electron density distribution for them, and the energies and compositions of some frontier orbitals are listed in Table 4.



Figure 5 Representation of calculated Kohn-Sham orbitals of L^1 and L^2 (TD-DFT/B3LYP).

| Compound | λ (nm) | E(eV) | f | Composition |
|----------|----------------|-------|--------|---------------------------|
| L^1 | 364.14 | 3.81 | 0.6337 | 132→133 (H→L)(0.67365) |
| | 345.58 | 4.06 | 0.2109 | 132→135 (H→L+2)(0.65386) |
| | 290.40 | 4.70 | 0.1904 | 132→136 (H→L+3)(0.41562) |
| L^2 | 381.36 | 3.63 | 0.4036 | 133→134 (H→L)(0.67841) |
| | 295.03 | 4.80 | 0.2124 | 132→134 (H–1→L)(0.57483) |

According to the calculated results, it is easily confirmed that the substituent -CHO in L^1 is involved in the whole electronic delocalization process. One of the bands is at 345.58 nm, HOMO to LUMO+2, consistent with the experimental results that a shoulder band appears in the linear absorption band of the chromophore L^1 . The other two transition bands exist at the position of 364.14 nm and 290.40 nm, respectively. The former band assigned as ICT with lower energy is derived from the transition of HOMO \rightarrow LUMO. The latter, at shorter wavelengths, may be related to the absorption of the triphenylamine moiety, corresponding to the composition of HOMO to LUMO+3.

Compared with L^1 , the -CH₂OH unit in L^2 has seldom contribution to the electron density distribution, although the absorption spectra of the investigated chromophores show similar features. There exist only two transition bands based on the theoretical calculation for L^2 . The lower energy excitation band at 381.36 nm is mainly assigned as ICT, which originates from the HOMO→LUMO transition. Interestingly, this band position is nearly 17 nm red-shifted compared with that of L^1 . The result can be not only reasonably explained by TD-DFT calculations of the lowest excited state energy (HOMO→LUMO), but also be powerfully confirmed by the experimental linear absorption spectra of chromophores, \mathbf{L}^1 and \mathbf{L}^2 . The remaining band ($\lambda_{max} =$ 295.03 nm, f = 0.21) is ascribed to local transition of the triphenylamine moiety as a result of the HOMO-1 \rightarrow LUMO transition.

3.3.3 Single-photon excited fluorescence (SPEF)

The single-photon excited fluorescence (SPEF) spectra were measured in the same concentrations in seven different organic solvents as those of the linear absorption spectra at their maximum excitation wavelengths. The SPEF spectra of L^2 and $L^{0,1}$ are shown in Figures 6 and S2, respectively. Related photophysical data of L^{0-2} , including fluorescence quantum yields ($\Phi_{\rm f}$), non/radiative rate constant ($k_{\rm r}$, $k_{\rm nr}$), Stokes' shift and fluorescence lifetimes (τ) (Figures 7 and S3) are collected in Table 3.

The figures show that SPEF spectra of all the chromo-

phores present remarkable bathochromic shifts with increasing polarity of the solvents. The maximum emission wavelength of L^0 is shifted by 55 nm from 430 nm in benzene to 485 nm in DMF, while that of L^1 is shifted by 44 nm from 452 nm in benzene to 496 nm in DMF, that of L^2 is shifted by 58 nm (438 nm in benzene and 496 nm in DMF). This suggests that the fluorescent exited state (defined as the first exited state, S1) of the molecule should possess larger dipole moment than that of the ground state. The dipole-dipolar interactions between the solute and solvent increase, leading to a more significant energy level decrease for the exited state [39]. Besides, the Stokes' shift was also calculated (Table 3), which can further demonstrate the influence of the solvent on fluorescence.

The fluorescence quantum yields (Φ_f), listed in Table 3, were measured by using quinine sulfate as the standard [40]. The fluorescence quantum yields of L^{0-2} change significantly with different polar solvents. Higher $\Phi_{\rm f}$ values are obtained in non-polar solvents with the highest $\Phi_{\rm f}$ values observed in C₆H₆. The order of $\Phi_{\rm f}$ values is L² (0.95) > L⁰ $(0.65) > L^{1}(0.33)$ in the benzene solution. It implies that the introduction of the group -CH₂OH helps to decrease the nonradiative decay pathways, and enhance the fluorescence quantum yields. However, the -CHO group has the opposite effect to that of the -CH₂OH. To further confirming this deduction, the rate constants for radiative (k_r) and nonradiative (k_{nr}) decays were calculated with reference to the Method A (Supporting Information). From the Table 3, the value k_r of \mathbf{L}^2 in benzene is apparently higher than that of the other chromophores.

3.4 Two-photon excited fluorescence (TPEF) and theoretical calculation of TPA cross sections (δ)

3.4.1 Two-photon excited fluorescence (TPEF)

As shown in Figure 4, there is no linear absorption in the range 600-880 nm for L⁰⁻², indicating that there are no energy levels corresponding to one electron transition in the spectral range. Therefore, upon excitation from 600 to 880 nm, it is impossible to produce single-photon excited



Figure 6 (a) Single-photon excited fluorescence of L^2 in seven selected solvents with a concentration of 1.0×10^{-5} mol L^{-1} ; (b) fluorescence emission photographs of \mathbf{L}^2 in seven selected solvents.

(a)



Figure 7 Time-resolved fluorescence curves of L^2 in seven selected solvents.

up-converted fluorescence [41].

While keeping the input power at the intensity of 500 mW, we recorded the TPEF intensities, which were measured by tuning the pump wavelength increment at 10 nm from 690 to 850 nm, and the TPEF spectra were obtained (Figures 8 and S4). Figures 9, 10 and S5 show the logarithmic plots of the fluorescence integral versus pumped powers

From Figures 11(a) and S6, at the optimal excited wavelength, for example, it can be found that the TPEF spectra of the chromophores in four different solvents present positive solvatochromism, the same trend as the one-photon fluorescence. The phenomenon may be contributed to the similarly vibronic structures in the TPEF and SPEF spectra of the chromophores [42]. It can be found that the highest intensity of the TPEF exists in the high polar solvent DMF, especially for that of L^2 . Figure 11(b) shows the TPEF of L^{0-2} at the excited wavelength in DMF solution. The intensities of TPEF of the three are in the sequence of $L^2 > L^0 >$ L^1 . Based on the principle, the smaller the energy gap is, the higher the possibility of the two-photon excitation is. The sequence is in complete consistency with DFT calculation, which is 3.63 eV (L^2), 3.75 eV (L^0), and 3.81 eV (L^1) about the energy gap of the three chromophores, respectively.

TPA cross sections (δ) of \mathbf{L}^{0-2} (Figure S7) have been obtained in four different polar solvents using the **Method B** given in Supporting Information. Figure 12 shows the TPA cross-section per molecular weight (δ_{max}/MW) of the chromophores in DMF. The maximum δ_{max}/MW values at the excitation wavelength are 0.53 GM/(g mol) (\mathbf{L}^{0}), 0.63



Figure 8 Two-photon fluorescence spectra of L^1 and L^2 in DMF pumped by femtosecond laser pulses at 500 mW at different excitation wavelengths.



Figure 9 (a) TPEF spectra of \mathbf{L}^1 under different pumped powers at 710 nm, with $c = 1.0 \times 10^{-3}$ mol \mathbf{L}^{-1} in DMF; (b) output fluorescence (I_{out}) vs. the square of input laser power (I_{in}) for \mathbf{L}^1 .



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Figure 10 (a) TPEF spectra of L^2 under different pumped powers at 760 nm, with $c = 1.0 \times 10^{-3}$ mol L^{-1} in DMF; (b) output fluorescence (I_{out}) vs. the square of input laser power (I_{in}) for L^2 .



Figure 11 (a) Two-photon fluorescence spectra of L^2 in different solvents with the same concentration of 1.0×10^{-3} mol L^{-1} in $\lambda_{em} = 760$ nm; (b) two-photon fluorescence spectra of L^{0-2} in DMF (1.0×10^{-3} mol L^{-1}) at excited wavelength.



Figure 12 TPA cross-section per molecular weight (δ /MW) of L⁰⁻² in DMF vs. excitation wavelengths of identical energy of 500 mW.

GM/(g mol) (L^1) and 0.72 GM/(g mol) (L^2), respectively. L^2 has the largest δ_{max}/MW value, indicating that the -CH₂OH group has been involved in the conjugated system of the molecule to some extent and provides some electrons to the whole system, which may increase the ICT. However, the substituent -CHO of L^1 , due to its medium electron withdrawing, may decrease the ICT efficiency. Therefore, L^1 has a lower δ_{max}/MW value than that of L^2 .

3.4.2 Theoretical calculation of TPA cross sections (δ)

To obtain more information about relationships between the structure and TPA properties, theoretical calculation of TPA cross sections (δ) was performed on equilibrium geometries of molecules (\mathbf{L}^1 and \mathbf{L}^2) using the DALTON 2011 program [43] in gas phase optimized by Gaussian package [38] at the hybrid density functional theory (DFT/B3LYP) level with 6-31G* basis set. The TPA cross section, which can be directly compared with the experimental results, is defined as the following equation:

$$\sigma_{\rm tp} = \frac{4\pi^2 a_0^5 \alpha}{15c_0} \times \frac{\omega^2 g(\omega)}{\Gamma_{\rm f}} \delta_{\rm tp} \tag{1}$$

In this equation, 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 spectral line profile, which is assumed to be a δ function here, and Γ_f is the lifetime broadening of the final state, which is commonly assumed to be 0.1 eV [44]. δ_{tp} is written as follows [45],

$$\delta_{\rm tp} = \sum_{\alpha\beta} [F \times S_{\alpha\alpha} \times S_{\beta\beta}^* + G \times S_{\alpha\beta} \times S_{\alpha\beta}^* + H \times S_{\alpha\beta} \times S_{\beta\alpha}^*] \quad (2)$$

Here F, G, and H are coefficients dependent on the polarization of the light. $S_{\alpha\beta}$ is the TPA transition matrix element. For the absorption of two photons with the same frequency $\omega_{\rm f}/2$, it can be written as [46],

$$S_{\alpha\beta} = \sum_{i} \left[\frac{\langle 0|\mu_{a}|i\rangle\langle i|\mu_{\beta}|f\rangle}{\omega_{i} - \omega_{i}/2} + \frac{\langle 0|\mu_{\beta}|i\rangle\langle i|\mu_{a}|f\rangle}{\omega_{i} - \omega_{i}/2} \right]$$
(3)

Here ω_i and ω_f are 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 nonlinear optical data of the three chromophores (\mathbf{L}^{0} , \mathbf{L}^{1} and \mathbf{L}^{2}) in gas phase are listed in Table 5, from which the calculated optical properties depending on the different geometries can be observed readily. The largest TPA cross section of the molecules is 262.77 for \mathbf{L}^{0} , 265.38 for \mathbf{L}^{1} , and 285.64 GM for \mathbf{L}^{2} (1 GM = 10⁻⁵⁰ cm⁴ s/photon). It is apparent that the theoretical calculation is consistent with the experimental result trend ($\mathbf{L}^{2} > \mathbf{L}^{1} > \mathbf{L}^{0}$) shown in Figures 12 and S7.

Table 5 Two-photon absorption cross-section $\delta_{\rm p}$ (1 GM = 10⁻⁵⁰ cm⁴ s/photon) of the three lowest exited states with the excitation energy *E* (eV) and the corresponding wavelength $\lambda_{\rm tp}$ (nm) in the gas phase

| L ^{0 a)} | Ε | 3.39 | 3.40 | 4.01 | 4.14 | 4.19 | 4.28 |
|-------------------|-------------------|--------|--------|--------|--------|--------|--------|
| | $\lambda_{ m tp}$ | 729.53 | 727.38 | 616.73 | 597.37 | 590.24 | 577.83 |
| | $\delta_{ m tp}$ | 262.77 | 0.04 | 0.19 | 18.33 | 23.54 | 0.00 |
| \mathbf{L}^{1} | Ε | 3.46 | 3.62 | 3.76 | 3.85 | 4.09 | 4.23 |
| | $\lambda_{ m tp}$ | 714.77 | 683.18 | 657.74 | 642.36 | 604.67 | 584.66 |
| | $\delta_{ m tp}$ | 265.38 | 0.39 | 127.22 | 0.29 | 7.49 | 0.14 |
| L^2 | Ε | 3.25 | 3.41 | 3.99 | 4.12 | 4.15 | 4.28 |
| | $\lambda_{ m tp}$ | 760.96 | 725.25 | 619.82 | 600.27 | 595.93 | 577.83 |
| | $\delta_{ m tp}$ | 285.64 | 0.04 | 0.13 | 39.93 | 19.81 | 0.03 |

a) The data of two-photon absorption cross-section $\delta_{\rm tp}$ cited from the Ref. [30].

4 Conclusion

Two novel D-A triphenylamino terpyridine derivatives (L^1 and L^{2}) were facilely synthesized *via* formylation and reduction. Based on the experimental and theoretical investigation, the structure-property relationships were established. The two chromophores showed apparent positive solvatochromism in various solvents mainly due to the ICT. Because of their almost approximate molecular volume and production costs, the TPA cross-section per molecular weight (δ_{max}/MW) was selected to compare NLO data. In high polar solvent DMF, the δ_{max}/MW of the chromophores is 0.63 GM/(g mol) (L^1) and 0.72 GM/(g mol) (L^2), respectively. Furthermore, it was readily found that the EDG, -CH₂OH can increase the ICT, which had the same direction of charge transfer in the whole molecule. However, compared with the -CH2OH, the EWG, -CHO had almost contrary effect, leading to decrease of the ICT. Therefore, the findings also implied that relatively large TPA cross section may be obtained by subtle modification rather than extending conjugated length over complicated organic synthesis.

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Appendix A. Supplementary data

CCDC 85415 and 90578 contain the supplementary crystallographic data for L^1 and L^2 , respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/ conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc. cam.ac.uk.

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