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Two-photon absorption in V-type chromophores with electron-rich heterocyclevinylene bridges

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A series of V-type chromophores with electron-rich heterocyclevinylene bridges have been synthesized via Wittig-Horner-Emmons and Vilsmeier reactions. All the target chromophores showed strong one-photon and two-photon excited emission, and their electron properties could be tuned by using different heterocycles such as furan, thiophene and pyrrole moieties in **I**–**III**. The maximum two-photon absorption (TPA) cross sections occurred at 760 nm and were measured to be in the range of 400–800 GM.

two-photon absorption, electron-rich, heterocycle, chromophore

1 Introduction

There is much interest in the development of organic conjugated materials with large two-photon absorption (TPA) cross sections (σ) as promising candidates for potential applications in a number of new areas, including the fluorescence imaging of biological samples, optical limiting, photodynamic therapy, three-dimensional optical data storage and micro-fabrication [1–5]. Organic conjugated molecules generally provide large electron delocalization of the π electrons throughout the whole molecule, which would be beneficial to the enhancement of the σ value. Many reports proposed various design strategies for efficient TPA molecules by a systematic variation of chromophores with various electron-donor (D) and electron-acceptor (A) moieties, which were attached symmetrically or unsymmetrically to a conjugated electron bridge (π) [6–12]. The effects of varying the electron-donating or electron-acceptor strength of end groups can vary the charge distribution, and the property and length of the conjugated electron bridge can modulate the electronic communication between the D or A moieties.

Among the various conjugated bridges, the extensively utilized π-centers were benzene, biphenyl, fluorene, and dihydrophenathrene, with simple functionalities such as OR, NR_2, NO_2, and CN bonded to them. Their electron properties could be tuned, and the π-centers with different electronic properties played an important role in enhancing the charge transfer in the TPA chromophores. Also, various heterocycles with electron-rich or electron-deficient properties were employed, which act as efficient auxiliary donor or acceptor moieties [13–16]. Furthermore, the intrinsic tunable nature of the heterocycles rings made these systems particularly appropriate to finely control the electronic and optical properties. The electron-rich heterocycles, such as furan, pyrrole and thiophene, have frequently been incorporated into the conjugated bridges of TPA chromophores. Albert *et al.* pointed out that electron-rich heterocycles exhibited a lower tendency to deplete charge from donor sub-

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*Corresponding author (email: lizhen@whu.edu.cn) stituents and hence increase the donor ability [17]. Marder's group reported that the TPA chromophores in which vinylene units and either pyrrole or dialkoxythiophene groups form the bridge between two diarylaminophenyl groups with D-π-D type exhibited high two-photon cross-sections [18].

In this work, we extended the study on the V-type TPA chromophores with the electron-rich five-member hetercycles furan, pyrrole and thiophene incorporated as the conjugated bridges (Chart 1), and triphenylamine moieties as the core or the donor group. Compared with the linear chromophores with plane configuration, the V-type chromophores which incorporated triphenylamine with propeller-shape and bulky volume as the core bridge, would benefit to the prevention of possible aggregation. The details of the synthesis, characterization, and optical properties were presented. The results suggested that the heterocycles with electron-rich properties as the conjugated bridges would be beneficial to the enhancement of the TPA cross section, however, the trend did not always accord well with the enhancement of the electron-rich properties.

2 Experimental

2.1 Materials

Tetrahydrofuran (THF) was dried over and distilled from K-Na alloys under an atmosphere of dry argon. *N*,*N*-Dimethylformamide (DMF) was dried over and distilled from CaH_2 under an atmosphere of dry argon. 1,2-Dichloroethane was dried over and distilled from phosphorus pentoxide. Phosphorus oxychloride was freshly distilled before use. Ethanol was dried over and distilled from sodium. 4-(Diphenylamino)benzaldehyde, diethyl 4-(diphenylamino)benzylphosphonate and *N*-hexylpyrrole-2-carbaldehyde were prepared following the procedure reported in refs. [19–20]. All other reagents were used as received.

2.2 Instruments

^1H and ^{13}C NMR spectroscopy study was conducted with a Varian Mercury 300 spectrometer using tetramethylsilane (TMS; $\delta = 0$ ppm) as internal standard. UV-vis spectra were obtained using a Shimadzu UV-2550 spectrometer. Photoluminescence spectra were performed on a Hitachi F-4500 fluorescence spectrophotometer. Matrix-assisted laser desorption ionization time-of-flight mass spectra were measured on a Voyager-DESTR MALDI-TOF mass spectrometer (MALDI-TOF MS; ABI, American) equipped with a 337 nm nitrogen laser and a 1.2 m linear flight path in positive ion mode, or a GCT premier CAB048 mass spectrometer. A mode-locked Ti:sapphire laser (Mai Tai, Spectra-Physics Inc.) was used as the excitation source. The average output power, pulse width, and repetition rate were 1.5 W, 100 fs, and 80 MHz, respectively. After passing through a circular variable neutral density filter that was used to control the power of the laser, the laser was focused into the cell (polished on all sides) by a focusing lens ($f = 6$ cm). The emission light was collected by an objective lens (10, NA = 0.3, Olympus, Japan) and then was focused by another objective lens (10, NA = 0.25, DHC, China) into a fiber optic spectrometer (USB2000, Ocean Optics Inc.), which was used to record the fluorescent spectra. Fluorescein in water was chosen as the reference standard.

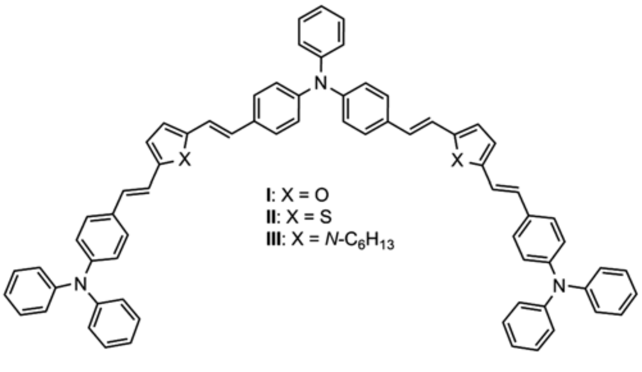


Chart 1

Synthesis of compound **2**

A solution of compound **1** (4.97 g, 16.5 mmol) and $NaBH_4$ (1.25 g, 33.0 mmol) was suspended in the mixture solvents of ethanol (10 mL) and THF (20 mL) at 40 °C overnight. The mixture was poured into ice cold water and extracted with chloroform for several times, the organic fractions were collected and dried over Na_2SO_4. The solvent was removed under reduced pressure to yield pure compound **2** (5.03 g, 100%). ^1H NMR ($CDCl_3$) δ (ppm): 7.23–7.17 (m, ArH, 5H), 7.06–6.98 (m, ArH, 8H), 4.59(s, 4H, –CH2–).

Synthesis of compound **3**

Compound **2** (5.03 g, 16.5 mmol) was dissolved in triethyl phosphate (39.15 g, 214.5 mmol), and the solution was cooled to 0–5 °C in an ice bath. Then iodine (8.38 g, 33.0 mmol) was added in batches. The resultant mixture was stirred at room temperature for 48 h. After the residual triethyl phosphate was removed under reduced pressure, the mixture was washed with water and extracted with chloroform for several times, the organic fractions were collected and dried over Na_2SO_4. The crude product was purified by column chromatography on silica gel using petroleum/ethyl acetate (6/1) as eluent to afford a white solid **3** (5.89 g, 65.4%). ^1H NMR ($CDCl_3$) δ (ppm): 7.22–7.16 (m, ArH, 5H), 7.04–6.98 (m, ArH, 8H), 4.08–3.99 (m, $-OCH_2-$, 8H), 3.09 (d, 4H, $J = 21.3$ Hz, $-CH_2-$), 1.25 (t, 12H, $J = 7.5$ Hz, $-CH_3$).

General procedure for the synthesis of compounds **4–6**

Compound **3** (1 equiv) was suspended in anhydrous tetrahydrofuran under an atmosphere of dry argon, *t*-BuOK (2 equiv) was added directly as a solid and the resultant mixture was stirred at room temperature for 10 min. After the addition of the solution of the required aldehyde (**2** equiv) in anhydrous tetrahydrofuran dropwise, the reaction mixture was stirred at room temperature overnight, then poured into water, The organic product was extracted with chloroform for several times, and dried over anhydrous Na_2SO_4. After removing the solvent, the crude products were purified through a silica gel chromatography column by using petroleum/ethyl acetate (10/1) as eluent.

Compound **4**: Compound **3** (1.10 g, 2.00 mmol), furan-2-carbaldehyde (0.39 g, 4.00 mmol) and *t*-BuOK (0.45 g, 4.00 mmol). Yellow oil (0.59 g, 68.7%). ^{1}H NMR ($CDCl_3$) δ (ppm): 7.38–7.26 (m, 13H, ArH), 7.12 (d, 1H, $J = 7.2$ Hz, ArH), 7.05 (d, 3H, $J = 8.7$ Hz, ArH), 6.98 (d, 2H, $J = 15.9$ Hz, –CH=CH–), 6.79 (d, 2H, $J = 16.8$ Hz, –CH=CH–), 6.41 (s, 1H, ArH), 6.31 (d, 2H, $J = 3.0$ Hz, ArH).

Compound **5**: Compound **3** (1.10 g, 2.00 mmol), thiophene-2-carbaldehyde (0.45 g, 4.00 mmol) and *t*-BuOK (0.45 g, 4.00 mmol). Yellow oil (0.54 g, 58.6%). ^{1}H NMR ($CDCl_3$) δ (ppm): 7.35 (d, 4H, $J = 8.7$ Hz, ArH), 7.31–7.26 (m, 3H, ArH), 7.18–7.11 (m, 5H, ArH), 7.07–6.98 (m, 9H, ArH and –CH=CH–), 6.88 (d, 2H, $J = 16.2$ Hz, –CH=CH–).

Compound **6**: Compound **3** (1.10 g, 2.00 mmol), *N*-hexylpyrrole-2-carbaldehyde (0.72 g, 4.00 mmol) and *t*-BuOK (0.45 g, 4.00 mmol). Yellow oil (0.75 g, 63.2%). ^{1}H NMR ($CDCl_3$) δ (ppm): 7.35–7.15 (m, 8H, ArH and –CH=CH–), 7.11–7.01(m, 9H, ArH and –CH=CH–), 6.84 (s, 5H, ArH), 6.16 (s, 1H, ArH), 3.95 (t, 4H, $J = 6.6$ Hz, –*N*–CH_2–), 1.75 (s, br, 4H, –CH_2–), 1.31 (s, br, 12H, –CH_2–), 0.88 (s, br, 6H, –CH_3).

General procedure for the synthesis of compound ***7–9***

DMF (3.0 equiv) was added to freshly distilled $POCl_3$ (2.4 equiv) under an atmosphere of dry argon at 0 °C, and the resultant solution was stirred until its complete conversion into a glassy solid. After the addition of a yellow solution of one of compound **4–6** (1.0 equiv) in 1,2-dichloroethane dropwise at 0 °C, the mixture was stirred at room temperature overnight, then poured into an aqueous solution of sodium acetate (1 M), and stirred for another 2 h. The mixture was extracted with chloroform for several times, the organic fractions were collected and dried over Na_2SO_4. After removing the solvent under reduced pressure, the crude products were purified through a silica gel chromatography column.

Compound **7**: Compound **4** (0.59 g, 1.37 mmol), $POCl_3$ (0.50 g, 3.29 mmol) and DMF (0.30 g, 4.11 mmol). Yellow green solid (0.28 g, 43.0%). ^{1}H NMR ($CDCl_3$) δ (ppm): 9.57 (s, 1H, –CHO), 7.37–7.24 (m, 7H, ArH), 7.20–6.92 (m, 7H, ArH), 6.81 (d, 2H, $J = 15.9$ Hz, –CH=CH–), 6.68 (d, 2H, $J = 16.2$ Hz, –CH=CH–), 6.50 (s, br, 2H, ArH), 6.28 (s, 1H, ArH), 6.20 (s, 1H, ArH).

Compound **8**: Compound **5** (0.54 g, 1.17 mmol), $POCl_3$ (0.43 g, 2.81 mmol) and DMF (0.26 g, 3.51 mmol). Yellow green solid (0.33 g, 55.0%). ^{1}H NMR ($CDCl_3$) δ (ppm): 9.84 (s, 1H, –CHO), 7.65 (d, 1H, $J = 6.6$ Hz, ArH), 7.39 (d, 2H, $J = 2.1$Hz, ArH), 7.36 (d, 2H, $J = 2.4$ Hz, ArH), 7.33–7.26 (m, 2H, ArH), 7.16 (d, 3H, $J = 6.6$ Hz, ArH), 7.12–7.05 (m, 10H, ArH and –CH=CH–), 7.00 (t, 1H, $J = 4.5$ Hz, ArH), 6.89 (d, 1H, $J = 16.2$ Hz, –CH=CH–).

Compound **9**: Compound **6** (0.75 g, 1.26 mmol), $POCl_3$ (0.46 g, 3.02 mmol) and DMF (0.28 g, 3.78 mmol). Yellow green solid (0.37 g, 45.3%). ^{1}H NMR ($CDCl_3$) δ (ppm): 9.45 (s, 1H, –CHO), 7.39 (d, 4H, $J = 8.4$ Hz, ArH), 7.34–7.26 (m, 3H, ArH), 7.16–7.07(m, 8H, ArH and –CH=CH–), 6.92 (d, 2H, $J = 4.5$ Hz, ArH), 6.86 (d, 2H, $J = 16.2$ Hz, –CH=CH–), 6.55 (d, 2H, $J = 3.6$ Hz, ArH), 4.45 (t, 4H, $J = 8.4$ Hz, –*N*–CH_2–), 1.75 (s, br, 8H, –CH_2–), 1.31 (s, br, 12 H, –CH_2–), 0.86 (s, br, 6H, –CH_3).

General procedure for the synthesis of compound ***I–III***

4-(Diphenylamino)benzylphosphonate (1.0 equiv) was suspended in anhydrous tetrahydrofuran under an atmosphere of dry argon, *t*-BuOK (2.0 equiv) was added directly as a solid and the resultant mixture was stirred at room temperature for 10 min. After the addition of the solution of one of compound **7–9** (2.0 equiv) in anhydrous tetrahydrofuran dropwise, the reaction mixture was stirred at room temperature overnight, then poured into water. The organic product was extracted with chloroform for several times, and dried over anhydrous Na_2SO_4. After removing the solvent, the crude products were purified through a silica gel chromatography column by using petroleum/ethyl acetate (10/1) as eluent.

Compound **I**: Compound **7** (0.24 g, 0.50 mmol), 4-(diphenylamino)benzylphosphonate (0.40 g, 1.00 mmol), *t*-BuOK (0.11 g, 1.00 mmol). Yellow solid (0.10 g, 21.0%). ^{1}H NMR ($CDCl_3$) δ (ppm): 7.36 (d, 15H, $J = 8.1$ Hz, ArH), 7.13–7.04 (m, 28H, ArH), 6.76 (d, 4H, $J = 16.2$ Hz, ArH), 6.57 (s, 2H, ArH), 6.37 (d, 4H, $J = 15.6$ Hz, ArH). ^{13}C NMR ($CDCl_3$) δ (ppm): 147.7, 132.7, 129.5, 127.5, 125.6, 124.8, 123.6, 123.3, 122.6, 114.9, 111.0. MS (MALDI-TOF), *m/z* [M$^+$]: 967.20, calcd, 967.42.

Compound **II**: Compound **8** (0.21 g, 0.40 mmol), 4-(diphenylamino)benzylphosphonate (0.32 g, 0.80 mmol), *t*-BuOK (0.09 g, 0.80 mmol). Yellow solid (78.3 mg, 19.6%). ^{1}H NMR ($CDCl_3$) δ (ppm): 7.33 (t, 8H, $J = 6.6$ Hz, ArH), 7.25 (t, 8H, $J = 7.2$ Hz, ArH), 7.15–6.99 (m, 27H, ArH and –CH=CH–), 6.90–6.81 (m, 10H, ArH and –CH=CH–). ^{13}C NMR ($CDCl_3$) δ (ppm): 148.6, 148.3, 148.1, 144.4, 143.1, 143.0, 132.7, 132.2, 130.5, 129.1, 128.9, 128.8, 128.4, 127.9, 126.8, 126.0, 125.7, 125.1, 124.6, 124.3, 121.6, 121.4.

Compound **III**: Compound **9** (0.20 g, 0.31 mmol), 4-(diphenylamino)benzylphosphonate (0.30 g, 0.75 mmol), *t*-BuOK (0.07 g, 0.62 mmol). Yellow solid (66.4 mg, 18.9%). ^{1}H NMR (CDCl$_3$) δ (ppm): 7.31–7.25 (m, 21H, ArH and –CH=CH–), 7.12–6.86 (m, 28H, ArH and –CH=CH–), 6.53 (s, br, 4H, ArH), 3.96 (s, br, 4H, –*N*–CH$_2$–), 1.66 (m, 4H, –CH$_2$–), 1.50 (s, br, 4H, –CH$_2$–), 1.25–1.03 (m, 8H, –CH$_2$–), 0.79 (s, br, 6H, –CH$_3$). ^{13}C NMR (CDCl$_3$) δ (ppm): 147.8, 133.3, 132.5, 129.4, 126.9, 125.9, 124.5, 124.3, 124.1, 123.1, 115.6, 107.4, 31.6, 29.9, 26.7, 22.7, 14.2. MS (MALDI-TOF), *m/z* [M$^+$]: 1133.1464, calcd, 1133.6335.

3 Results and discussion

3.1 Synthesis and characterization

The synthetic route and chemical structures of the TPA chromophores (**I–III**) are shown in Scheme 1. For the unique configuration of triphenylamine, compound **3** was synthesized as the π-center of the V-type chromophores in two-step sequences: the deoxidization of the aldehyde group in compound **1**, and then followed by the reaction with triethyl phosphate. The heterocyclevinylene-containing building blocks of **4–6** were obtained by means of a double Wittig-Horner-Emmons olefination of compound **3** and the required aldehydes in the presence of *t*-BuOK in THF with satisfactory yields from 58.6% to 68.7%. The conversion of compound **4–6** to the corresponding bisaldehydes **7–9** was achieved by the Vilsmeier reaction. In the case of this reaction, it was possible that the aldehyde group could be introduced to triphenylamine moieties, thus leading to their relatively low yields. Finally, the TPA chromophores were yielded by the double Wittig-Horner-Emmons olefination of compound **7–9** and 4-(diphenylamino)benzylphosphonate. All the chromophores were soluble in common organic solvents such as THF, chloroform, DMF and DMSO and characterized by ^{1}H and ^{13}C NMR.

3.2 One-photon physical properties

The photophysical properties of **I–III** were investigated in dilute THF solutions, with their normalized absorption spectra depicted in Figure 1, and the corresponding photophysical data summarized in Table 1. All the TPA chromophores displayed an intense absorption in the UV-vis region, and the maximum of the absorption spectra could be tuned by the nature of heterocycles as the conjugated bridges. When the conjugated bridges changed from furylvinylene to thienylvinylene, chromophore **II** demonstrated much longer $\lambda_{\max}$, about 12 nm red-shifted than that of chromophore **I**, then changing the thiophene moiety with pyrrole one, the $\lambda_{\max}$ of chromophore **III** further red-shifted a little. Thus, the red-shift of the $\lambda_{\max}$ was along with the increasement of the electron-rich properties of the heterocycles, indicating that the electron-rich heterocycles as the conjugated bridges would be beneficial to the charge transfer in the whole molecules. Perhaps, the richer the electron lied in the Conjugated system, the better the charge transfer could take place. In addition, for the chromophores of V-type, there

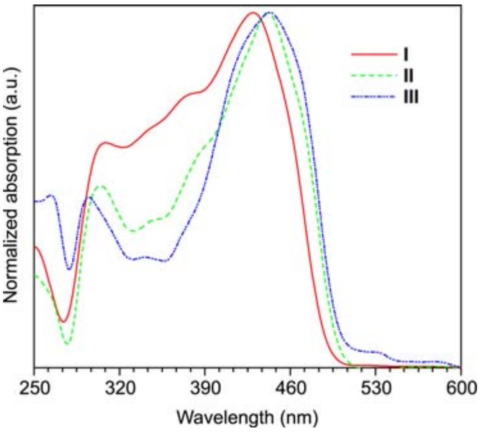
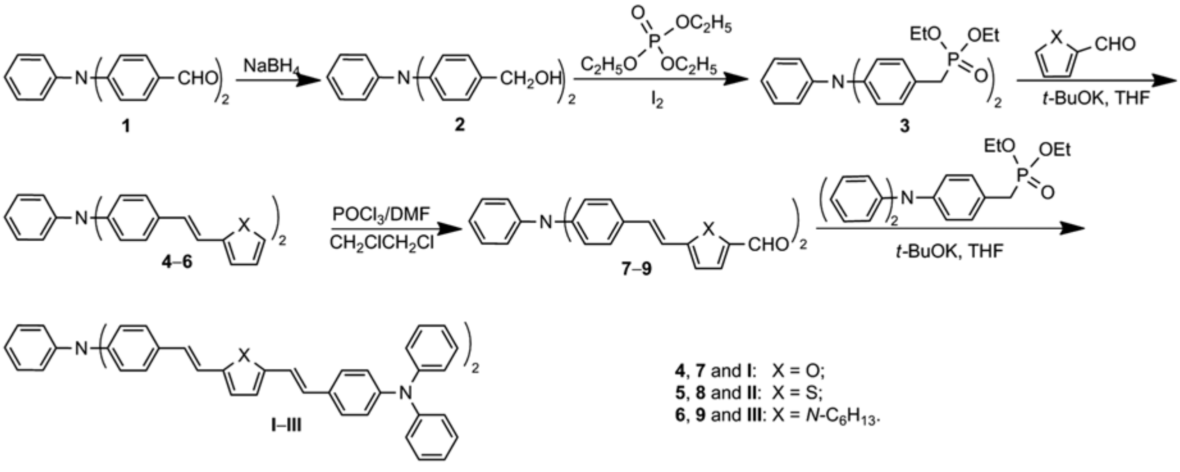


Figure 1 UV-vis spectra of the TPA chromophores **I–III** in THF solution. Concentration: 1.0×10^{-6} M.



Scheme 1

Table 1 Some photophysical data of chromophores

	$\lambda_{\max}^{\mathrm{ab}}$ (nm) a)	$\lambda_{\max}^{\mathrm{em}}$ (nm) b)	$\lambda_{\max}^{\mathrm{tp}}$ (nm) c)	Φ (%) d)	σ (GM) e)
I	429 (5.5×10^4)	487	760	66.3	625
II	441 (6.2×10^4)	503	760	50.8	777
III	444 (5.0×10^4)	499	760	76.7	441

a) 1.0×10^{-6} M in THF, wavelength of maximum absorbance and the value of molar absorptivity (ε, $\mathrm{cm^{-1}\cdot mol^{-1}\cdot L^{-1}}$) is given in parentheses. b) 1.0×10^{-6} M in THF, wavelength of maximum intensity. c) 2.0×10^{-5} M in THF, wavelength of maximum TPA cross sections. d) Quantum yields in THF solution using fluorescein in water (Φ=90%, pH 11) as a standard. e)TPA cross sections, 1 GM (Göppert-Mayer) = 10^{-50} $\mathrm{cm^4\cdot s\cdot photon^{-1}}$, the experimental uncertainty on $\sigma_{\max}$ is of the order of 10%–15%.

were double charge transfers from the donor groups to the π-center, resulting in the broad absorption and high molar extinction coefficients.

One-photon emission spectra of the TPA chromophores were demonstrated in Figure 2, with the data summarized in Table 1. The $\lambda_{\max}$ of the emission spectra shifted from 487 nm for chromophore **I** to 503 nm for chromophore **II** and 499 nm for chromophore **III,** respectively. The little blue-shifted emission wavelength of **III** in comparison with that of **II** was a little strange, indicating the special electronic properties of pyrrole moieties. In Figure 2, the different emission peak heights of the three chromophores reflected their different fluorescent emission quantum yields (Φ), as calibrated by using dye molecules with well established fluorescent emission quantum yields such as fluorescein. All of these three chromophores emitted green fluorescence and their Φ values ranged from 50.8% to 76.7%.

3.3 Two-photon absorption properties

The TPA cross sections (σ) were determined with the two-photon-induced fluorescence measurement technique by using femto-second laser pulses, which can avoid possible complications due to the excited-state excitation. In all cases, the output intensity of two-photon excited fluorescence was linearly dependent on the square of the input laser intensity, thereby confirming the TPA process (Figure 3).

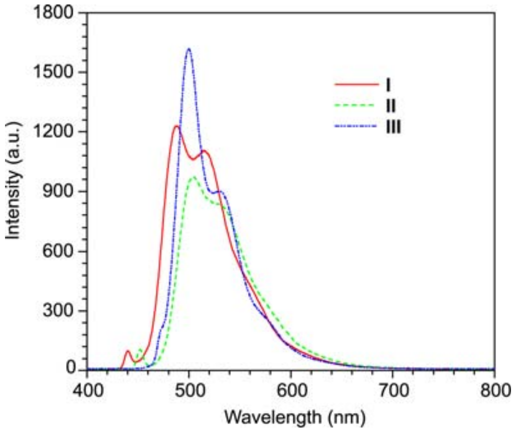


Figure 2 One-photon emission spectra of the TPA chromophores **I–III** in THF solution. Concentration: 1.0×10^{-6} M.

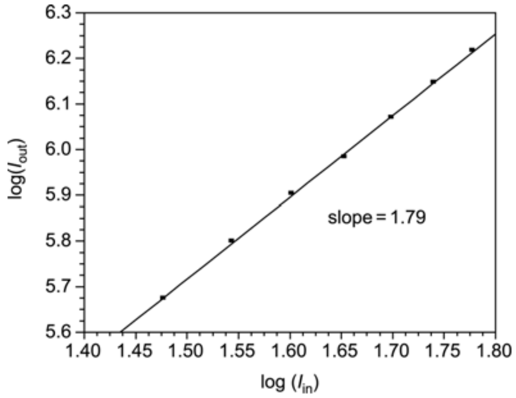


Figure 3 The dependence of logarithmic output fluorescence intensity (up-conversion signal) on logarithmic input laser power under the excited wavelength of 800 nm for chromophore **III**. Concentration: 2.0×10^{-5} M.

Typical two-photon absorption upconverted fluorescence signatures for chromophores are shown in Figure 4, and they exhibited strong two-photon excited emission. The two-photon-induced fluorescence signal was collected at the same detection wavelength for both the reference and sample compounds. The chromophores were stable under the experimental conditions described here, and no bleaching of the solutions was observed at the end of the measurement. The corresponding two-photon excitation spectra of compounds **I–III** in THF solution for excitation wavelengths ranging from 730 to 900 nm are shown in Figure 5. All the

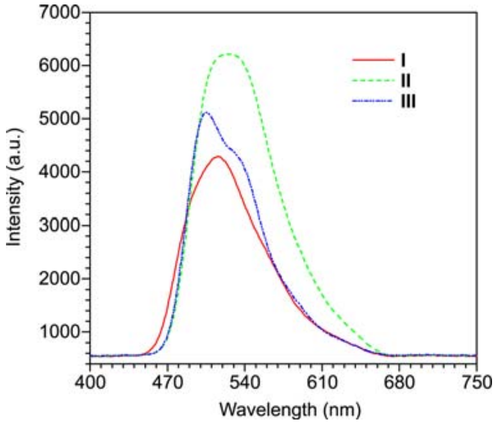


Figure 4 Two-photon-absorption-induced fluorescence emission spectra of chromophores in THF.

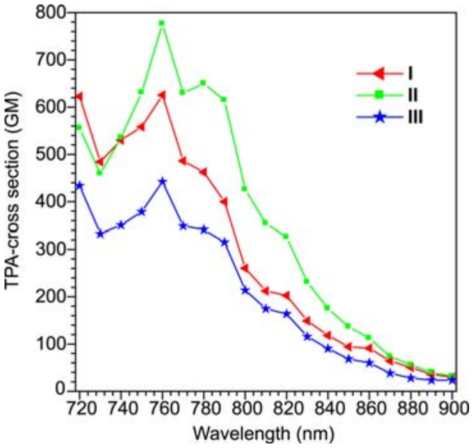


Figure 5 Two-photon absorption cross section (σ) of chromophores in THF.

chromophores exhibited modest to larger two-photon cross sections ranging from 441 to 777 GM at 760 nm. It was surprised that chromophore **III** with the most electron- rich hetercycle, pyrrole, as the conjugated bridge, exhibited the lowest σ value, not in accordance with the phenomena reported by Marder's group [18], that was, in the symmetrical linear D-π-D type chromophores, compared with the chromophores bearing pyrrole or dialkoxythiophene groups as the conjugated bridge between two diarylaminophenyl groups, the more electron-rich pyrrole examples showed the higher σ value, disclosing that the final properties of the chromophores were heavily dependent on the cooperation of each part of the whole molecule, but not some special part. The obtained results of the V-type and linear chromophores indicated that the charge transfer through the whole molecule was different. In the V-type chromophores, because of the nonplanar structure of the triphenylamine, the conjugated system did not well extend as that of the chromophores with the planar π-center, therefore, the effect of the electron-rich properties was not obvious as that in linear chromophores. Therefore, the interplay of torsional conformation is an important factor in the design of TPA chromophores with large two-photon cross sections.

4 Conclusions

In summary, we have introduced different electron-rich heterocyclevinylene bridges into the V-type chromophores, in which the triphenylamine moieties acted as the core or the donor group, and different heterocycles such as furan, thiophene and pyrrole groups as the π-bridge. As the unique configuration of the V-type molecules, the largest σ value was achieved in the chromophore with thienylvinylene bridges.

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1 Hales JM, Matichak J, Barlow S, Ohira S, Yesudas K, Brédas JL, Perry JW, Marder SR. Design of polymethine dyes with largethird-order optical nonlinearities and loss figures of merit. *Science*, 2010, 327: 1485–1488
2 Cumpston BH, Ananthaval SP, Barlow S, Dyer DL, Ehrlich JE, Erskine LL, Heikal AA, Kuebler SM, Lee IYS, McCord-Maughon D, Qin J, Röckel H, Rumi M, Wu XL, Marder SR, Perry JW. Two-photon polymerization initiators for three-dimensional optical data storage and microfabrication. *Nature*, 1999, 398: 51–54
3 Zhou WH, Kuebler SM, Braun KL, Yu T, Cammack JK, Ober CK, Perry JW, Marder SR. An effcient two-photon-generated photoacid applied to positive-tone 3D microfabrication. *Science*, 2002, 296: 1106–1109
4 Scott TF, Kowalski BA, Sullivan AC, Bowman CN, McLeod RR. Two-color single-photon photoinitiation and photoinhibition for subdiffraction photolithography. *Science*, 2009, 324: 913–917
5 LaFratta CN, Fourkas JT, Baldacchini T, Farrer RA. Multiphoton fabrication. *Angew Chem Int Ed*, 2007, 46: 6238–6258
6 Cho BR, Son KH, Lee SH, Young-Suk S, Lee YK, Jeon SJ, Choi JH, Lee H, Cho M. Two photon absorption properties of 1,3,5-tricyano-2,4,6-tris(styryl)benzene derivatives. *J Am Chem Soc*, 2001, 123: 10039–10045
7 Bartholomew GP, Rumi M, Pond SJK, Perry JW, Tretiak S, Bazan GC. Two-photon absorption in three-dimensional chromophores based on [2.2]-paracyclophane. *J Am Chem Soc*, 2004, 126: 11529–11542
8 Chung SJ, Rumi M, Alain V, Barlow S, Perry JW, Marder SR. Strong, low-energy two-photon absorption in extended amine-terminated cyano-substituted phenylenevinylene oligomers. *J Am Chem Soc*, 2005, 127: 10844–10845
9 Woo HY, Korystov D, Mikhailovsky A, Nguyen TQ, Bazan GC. Two-photon absorption in aqueous micellar solutions. *J Am Chem Soc*, 2005, 127: 13794–13795
10 Bordeau G, Lartia R, Metge G, Fiorini-Debuisschert C, Charra F, Teulade-Fichou MP. Trinaphthylamines as robust organic materials for two-photon-induced fluorescence, *J Am Chem Soc*, 2008, 130: 16836–16837
11 Lo PK, Li KF, Wong MS, Cheah KW. Synthesis and structure-linear and structure-nonlinear optical properties of multi-dipolar zigzag oligoaryleneethynylenes. *J Org Chem*, 2007, 72: 6672–6679
12 Yang WJ, Kim CH, Jeong MY, Lee SK, Piao MJ, Jeon SJ, Cho BR. Synthesis and two-photon absorption properties of 9,10-bis(arylethynyl) anthracene derivatives. *Chem Mater*, 2004, 16: 2783–2789
13 Liu ZQ, Shi M, Li FY, Fang Q, Chen ZH, Yi T, Huang CH. Highly selective two-photon chemosensors for fluoride derived from organic boranes. *Org Lett*, 2005, 7: 5481–5484
14 Liu ZQ, Fang Q, Cao DX, Wang D, Xu GB. Triaryl boron-based A-π-A vs. triaryl nitrogen-based D-π-D quadrupolar compounds for single- and two-photon excited fluorescence. *Org Lett*, 2004, 6: 2933–2936
15 Chung SJ, Kim KS, Lin TC, He GS, Swiatkiewicz J, Prasad PN. Cooperative enhancement of two-photon absorption in multi-branched structures. *J Phys Chem B*, 1999, 103: 10741–10745
16 Wang H, Li Z, Shao P, Qin J, Huang Z. Two-photon absorption property of a conjugated polymer: Influence of solvent and concentration on its property. *J Phys Chem B*, 2010, 114: 22–27
17 Albert IDL, Marks TJ, Ratner MA. Large molecular hyperpolarizabilities. quantitative analysis of aromaticity and auxiliary donor-acceptor effects. *J Am Chem Soc*, 1997, 119: 6575–6582
18 Zheng S, Beverina L, Barlow S, Zojer E, Fu J, Padilha LA, Fink C, Kwon O, Yi Y, Shuai Z, Stryland EWV, Hagan DJ, Brédas JL, Marder SR. High two-photon cross-sections in bis(diarylaminostyryl) chromophores with electron-rich heterocycle and bis(heterocycle) vinylene bridges. *Chem Commun*, 2007, 1372–1374
19 Li Q, Lu C, Zhu J, Fu E, Zhong C, Li S, Cui Y, Qin J, Li Z. Nonlinear optical chromophores with pyrrole moieties as the conjugated bridge: Enhanced NLO effects and interesting optical behavior. *J Phys Chem B*, 2008, 112: 4545–4551
20 Zheng SJ, Barlow S, Parker CT, Marder RS. A convenient method for the synthesis of electron-rich phosphonates. *Tetrahedron Lett*, 2003, 44: 7989–7992