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Synthesis, characterization, and nonlinear optical (NLO) properties of truxene-cored diphenylamine derivatives

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Abstract:

Three star-shaped compounds based on a truxene core (**FS11**, **FS12** and **FS13**) were prepared. The truxene core is incorporating with asymmetric diphenylamines, including one phenyl of diphenylamine substituted by methoxy group and the other phenyl substituted by tolyl, fluorophenyl and phenylethynyl for **FS11**, **FS12** and **FS13**, respectively. Their one-photon, two-photon absorption, geometric structures, electrochemical behavior and thermal properties were investigated. The absorption maxima of charge transfer band for **FS11**, **FS12** and **FS13** are 375 nm, 373 nm and 383 nm, and the corresponding molar extinction coefficients of **FS11**, **FS12** and **FS13** is 79950 M⁻¹cm⁻¹, 67220 M⁻¹cm⁻¹ and 108780 M⁻¹cm⁻¹. The "pull-push" structure promotes charge transfer between asymmetric diphenylamine branches and the truxene core. Their two-photon absorbtion property is measured by two-photon induced fluorescence. The maximum two-photon cross-sections values of **FS11**, **FS12** and **FS13** are excited at 750 nm, which are 260 GM, 204GM and 367 GM, respectively.

Keyword: Truxene; diphenylamine; asymmetric; two-photon absorption; two-photon induced fluorescence

1. Introduction

Nonlinear optical (NLO) materials with strong two-photon absorption (2PA) have attracted a great deal of attention in recent years [1-4]. Organic molecules and polymers have been developed [5-8], and their NLO and electronic properties have been investigated. A lot of work has been devoted in enhancing the 2PA property by strategy of molecular design. The 2PA behavior can be influenced by parameters such as molecular symmetry, molecular weight, and solubility [9]. Star-shaped organic molecules possessing extended π -conjugated construction exhibit excellent one-photon absorption, NLO and fluorescence emission properties, and thus they are widely used in organic light-emitting diodes [10], two-photon photodynamic therapy [11] and 3D optical data storage [12]. Star-shaped organic molecules consist of a central core and branches. Multi-branched π -conjugation structures enhance NLO response of star-shaped molecules, benefiting from enlarged electronic delocalization and increased intramolecular charge transfer [13, 14]. The introduction of electron donor and electron acceptor as end groups onto the branches symmetrically or unsymmetrically can further extend the electron-donating or electron-accepting strength and the conjugation length of star-shaped molecules, leading to increase 2PA cross-section $(\sigma 2)$ [14]. The flexibility on structure modification and facile synthesis provide a good basis for star-shaped organic π -conjugation molecules to be used in NLO devices.

Truxene (10, 15-dihydro-5H-diindeno[1,2-a;1',2'-c]fluorene) is a C₃-sythmmetric organic molecule, and it possesses satisfactory solubility, rigid

2-dimensinal structure, good thermal stability and ease to be modified [15, 16]. Truxene-cored materials have been widely used in organic light-emitting devices [17, 18], three-photon absorption [19], dye-sensitized solar cell [20] and perovskite solar cells [21, 22], two-photon absorption [23-26]. The good solubility of truxene-cored materials can be realized by attaching long alkyl chains on C9, C12 and C15 positions of truxene, as well as the restraint of molecule aggregation. Different branched moieties can be introduced onto the C2, C7, and C12 positions of the truxene core [23]. Chan and co-workers have studied 2PA properties of truxene-containing platinum (II) alkynyl complexes [23]. In their report, one complex incorporated with electron-deficient oxadiazole moiety gave the greatest σ^2 values of 51 GM at 720 nm, which create a large change in the dipole moment within the molecules. Lin and co-workers have reported a series of two-photon-active truxene-cored derivatives with varied number and size of functionalized pyrazine units [24]. The overall coplanarity between the central core and the "fusing" peripheral branches is improved, yielding a very active 2PA response up to 5100 GM at 730 nm. Yuan and co-workers have prepared three thiophenevinyl substituted one-, two-, and three-branched truxene π -conjugated compounds [25]. The σ 2 of three-branched compound (235 GM) is several times that of the two-branched compound (76 GM) and one-branched compound (27 GM). In addition, Zheng and co-workers have reported highly soluble π -conjugated turuxene-containing dendritic chromophores with large two-photon absorption in the range of 92.8-1412 GM [26]. In their research, diphenylamine was chosen as an electron donor and butyl groups were introduced for increasing

chromophore solubility in organic solvents. The dendritic or the three-branched chromophore with diphenylamine has both an extended π -conjugated system and an increased intramolecular charge redistribution compared to the one-branched chromophore. These results indicate that the star-shaped molecules can make a great contribution for obtaining strong 2PA absorption, and truxene is a promising building block for the construction of NLO materials. The three-branched truxene compounds can show a large π -conjugation length, and the introduction of appropriate electron donors or accepters onto branched chromophore can enhance 2PA capability.

In this paper, three truxene-cored compounds (FS11, FS12, and FS13) were synthesized by a facile route. The structures of FS11, FS12, and FS13 are shown in Fig.1. The whole molecule based on a truxene core is symmetric with a three-branched structure. The diphenylamine branch incorporating with the truxene core is asymmetric. For the studied compounds, one phenyl of diphenylamine is substituted by methoxy group, and the other phenyl of diphenylamine is substituted by tolyl for FS11, fluorophenyl for FS12 and phenylethynyl for FS13, respectively. The electron-donating -OMe on tolyl, the electron accepting -F on fluorophenyl and the extended π -conjugation -C=C- on phenylethynyl possibly have a great influence on their optical properties. Therefore, their one-photon and two-photon photophysical properties, geometric structure, energy levels and thermodynamic characters have been investigated. The results indicate these truxene-cored diphenylamine derivatives have a great potential in optical materials.



Fig. 1. The structures of FS11, FS12 and FS13.

2. Experimental

2.1. Materials and instruments

The solvents and chemicals used in this work were analytical grade and used without further purification and purchased from Energy Chemical (China). The reagents for reactions and spectral measurements were dried and distilled before use. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AM-300 or AM-400 spectrometer at 25 °C using DMSO-d₆ as solvent. The reported chemical shifts were against TMS. High resolution mass spectra were obtained with a Micromass GCT-TOF mass spectrometer. The melting point was taken on a RY-1 thermometer and the temperatures were uncorrected.

2.2. Spectral, electrochemical and thermal stability measurements

The absorption spectra of FS11, FS12, and FS13 in solution were measured by SHIMADZU UV-2600 spectrophotometer. Fluorescence measurements were carried out with a HITACHI F-4500 fluorescence spectrophotometer. The absolute fluorescence quantum yield was directly measured by a FLS980 fluorescence spectrometer at room temperature [27]. The corresponding concentration of FS11, **FS12**, and **FS13** is 5×10^{-7} mol L⁻¹ in dichloromethane, and Rhodamine B is used as a reference. Cyclic voltammetry (CV) measurements were performed on a Zennium electrochemical workstation (ZAHNER, Germany) using a three-electrode system. Tetrabutylammoniun hexafluorophosphate (n-Bu₄NPF₆) of 0.1 M was added into a dichloromethane solution (DCM) as electrolyte. The thermal stability was determined by thermogravimetry (TG) and differential scanning calorimetry (DSC). TG analyses were performed on TG 209 F3 Tarsus (NETZSCH, Germany) at a heating rate of 10 °C/min under a nitrogen atmosphere. DSC analyses were conducted on DSC 200 F3 Maia (NETZSCH, Germany) at a heating rate of 10 °C/min under a nitrogen atmosphere.

2.3. Synthesis

Compounds 1–3 and 4a-c were synthesized according to literature methods reported [22, 28-33] and the synthesis procedure of FS11, FS12 and FS13 is shown in Scheme 1.



Scheme 1. The synthetic route of FS11, FS12, and FS13.

2.3.1. General procedure for the synthesis of compounds **5a**, **5b** and **5c**

To a 100 mL two neck round-bottom flask were added compound **4c** (500.0 mg, 1.0eq), p-anisidine (287.2 mg, 1.2eq), $Pd_2(dba)_3$ (35.6 mg, 0.02eq), t-BuONa (280.1 mg, 1.5eq), P(t-Bu)_3 (7.9 mg, 0.02eq) and 10 mL anhydrous toluene. The reaction mixture was refluxed 12 h under argon. After cooling down to room temperature, the mixture was exacted with ethyl acetate and washed with water. The organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuum to give the crude product, which was purified by column chromatograph packed with silica gel using petroleum ether (PE)-ethyl acetate (EA) (100:1) as the eluent to afford pure compound **5c**.

5a: gray soild (421.2 mg, 72%), ¹H NMR (400 MHz, DMSO) δ 7.99 (s, 1H),
7.48 (d, J = 2.7 Hz, 2H), 7.46 (d, J = 3.2 Hz, 2H), 7.21 (d, J = 7.9 Hz, 2H), 7.08 (d, J = 8.9 Hz, 2H), 6.98 (d, J = 8.7 Hz, 2H), 6.89 (d, J = 8.9 Hz, 2H), 3.72 (s, 3H), 2.31 (s, 3H).

5b: yellow soild (367.7 mg, 63%), ¹H NMR (400 MHz, DMSO) δ 8.01 (s, 1H), 7.61 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.22 (t, *J* = 8.8 Hz, 2H), 7.09 (d, *J* = 8.9 Hz, 2H), 6.99 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.9 Hz, 2H), 3.73 (s, 3H).

5c: pale green soild (372.3 mg, 64%), ¹H NMR (400 MHz, DMSO) δ 8.24 (s, 1H), 7.49 (d, J = 6.4 Hz, 2H), 7.38 (t, J = 7.7 Hz, 3H), 7.34 (d, J = 8.6 Hz, 2H), 7.10 (d, J = 8.9 Hz, 2H), 6.89 (dd, J = 9.7, 10.3 Hz, 4H).

2.3.2 General procedure for the synthesis of FS11, FS12 and FS13

To a 100 mL two neck round-bottom flask were added compound **5c** (593.0 mg, 3.3eq), **3** (500.0 mg, 1.0eq), $Pd_2(dba)_3$ (55.0 mg, 0.1eq), t-BuOK (403.8 mg, 6.0eq), X-phos (57.3 mg, 0.2eq) and 10 mL anhydrous toluene. The reaction mixture was refluxed 12 h under argon. After cooling down to room temperature, the mixture was exacted with ethyl acetate and washed with water. The organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated in vacuum to give the crude product, which was purified by column chromatograph packed with silica gel using PE-EA (40:1) as the eluent to afford pure compound **FS13**.

FS11: Yellow powder (72% yield). M.p:178-180 °C. ¹H NMR (400 MHz, DMSO) δ
8.10 (d, J = 8.2 Hz, 3H), 7.56 (d, J = 8.5 Hz,6H), 7.53 (d, J = 8.2 Hz, 6H), 7.24 (d, J = 8.0 Hz, 6H), 7.20 (s, 3H), 7.14 (d, J = 8.8 Hz, 6H), 7.06 (d, J = 8.6 Hz, 6H), 6.98 (d, J

= 8.7 Hz, 6H), 6.95 (d, J = 8.4 Hz, 3H), 3.78 (s, 9H), 2.78–2.70 (m, 6H), 2.33 (s, 9H), 1.91–1.78 (m, 6H), 0.64–0.43 (m, 30H). ¹³C NMR (100 MHz, CDCl₃) δ 156.66, 155.07, 148.34, 145.72, 143.44, 140.16, 137.85, 135.36, 131.46, 127.68, 123,76, 121.58, 121.34, 117.39, 115.28, 114.93, 89.90, 88.49, 55.52, 39.18, 17.45, 14.60. HRMS (ESI) calcd for C₁₀₅H₁₀₅N₃O₃ (M⁺H⁺):1457.8268, found: 1457.8223.

FS12: Yellow powder (74% yield). M.p:167-169 °C. ¹H NMR (400 MHz, DMSO) δ 8.09 (d, J = 8.6 Hz, 3H), 7.65 (dd, J = 8.7, 5.5 Hz, 6H), 7.54 (d, J = 8.6 Hz, 6H), 7.24 (t, J = 8.8 Hz, 6H), 7.19 (s, 3H), 7.12 (d, J = 8.8 Hz, 6H), 7.04 (d, J = 8.6 Hz, 6H), 6.97 (d, J = 9.0 Hz, 6H), 6.93 (d, J = 7.3 Hz, 3H), 3.76 (s, 9H), 2.79–2.65 (m, 6H), 1.90–1.76 (m, 6H), 0.63–0.41 (m, 30H). ¹³C NMR (100 MHz, CDCl₃) δ 163.37, 160.92, 156.36, 155.05, 147.67, 146.19, 143.17, 140.70, 136.93, 134.91, 133.28, 128.04, 127.38, 125.25, 122.72, 120.98, 116.88, 115.68, 115.46, 114.85, 55.53, 39.21, 17.46, 14.63. HRMS (ESI) calcd for C₁₀₂H₉₆F₃N₃O₃ (M⁺H⁺):1469.7475, found: 1469.7469.

FS13: Fluorescence green powder (71% yield). M.p:177-179 °C. ¹H NMR (400 MHz, DMSO) δ 8.15 (d, *J* = 8.0 Hz, 3H), 7.50 (d, *J* = 5.3 Hz, 6H), 7.40 (d, *J* = 6.9 Hz, 15H), 7.28 (s, 3H), 7.16 (d, *J* = 8.7 Hz, 6H), 7.00 (d, *J* = 8.7 Hz, 9H), 6.92 (d, *J* = 8.6 Hz, 6H), 3.78 (s, 9H), 2.81–2.69 (m, 6H), 1.95–1.82 (m, 6H), 0.66–0.40 (m, 30H). ¹³C NMR (100 MHz, CDCl₃) δ 156.25, 155.03, 147.40, 146.28, 143.10, 140.84, 137.95, 136.38, 134.80, 134.32, 129.47, 127.31, 125.21, 122,82, 120.86, 116.78, 114.81, 55.53, 55.48, 39.20, 21.07, 17.45, 14.63. HRMS (ESI) calcd for C₁₀₈H₉₉N₃O₃ (M⁺H⁺):1487.7728, found: 1487.7753.

The ¹H NMR and ¹³C NMR of compounds **FS11**, **FS12** and **FS13** are given in the supplementary materials.

2.4. Two-photon absorption measurements

The σ^2 values of the three compounds have been measured with the two-photon-induced fluorescence (2PEF) method by using the femto-second laser pulses as described [34]. The 2PEF spectra were recorded on SD2000 spectrometer (Ocean Optical) with excitation with a femtosecond laser (Tsunami, Spectra-Physics). This laser provided pulses of 100-fs of duration at a repetition rate of 80 MHz and was tunable in the wavelength range of 720-880 nm. The laser beam was focused into a quartz cell of 1 cm path length by using a 5 cm focal-length lens. To calculate the 2PEF cross sections, Rhodamine B in methanol solution ($1 \times 10^{-6} \text{ mol L}^{-1}$) was utilized as reference for the calculation. For all the products, an acetonitrile solution ($1 \times 10^{-5} \text{ mol L}^{-1}$) was prepared to calculate the 2PEF cross sections. The fluorescence quantum yields of **FS11**, **FS12**, **FS13** and Rhodamine B are 0.2369, 0.2323, 0.3562 and 0.3977, respectively. All the samples and reference were tested under the same experimental conditions.

The 2PEF cross sections were then calculated by the equation (1):

$$\sigma_{TPEF} = \frac{\Phi_{ref} c_{ref} n_{ref} F}{\Phi_{cn} F_{ref}} \sigma_{ref}$$
(1)

where *c* and Φ were the concentration and the fluorescence quantum yield of the samples (**FS11**, **FS12** and **FS13**) and reference (Rhodamine B), and *n* was refractive index of the solvents. *F* was the integral of the TPEF spectrum. The σ_{ref} value of reference was taken from the literature [35].

3. Results and discussion

The synthetic procedure of **FS11**, **FS12** and **FS13** was showed in Scheme 1. 2,7,12-tribromo-5,5',10,10',15,15'-hexapropyltruxene (compound **3**) was obtained by compound **1** reacted with Bromopropane, n-BuLi and a bromination reaction. Then, compound **5** was prepared by compound **4** reacting with p-methoxyaniline via a Buchwald-Hartwig reaction. Finally, the target compound **FS11** was synthesized by Buchwald-Hartwig reaction of **3** with **5**. **FS12** and **FS13** were synthesized by similar procedures. All the intermediates and target dyes were purified and identified by NMR spectra. The UV-vis absorption and fluoresce emission spectra, and electrochemical data of **FS11**, **FS12** and **FS13** were also measured, respectively.

3.1. One-photon absorption and emission properties

The one-photon absorption and fluorescence emission properties of FS11, FS12 and FS13 in dichloromethane are shown in Fig. 2, and the corresponding spectroscopic data are summarized in Table 1. Three compounds have a strong absorption at the region of 250-400 nm, and the maximum absorption wavelengths (λ_{max}) of FS11, FS12 and FS13 are 375 nm, 373 nm and 383 nm, respectively. The absorption band at 260-280 nm can be attributed to π - π * transitions, while the band at 350-380 nm is mainly corresponding to the intramolecular charge transfer (ICT) from the diphenylamine to the truxene core [36]. A red-shifted absorption band of FS13 is observed, due to the introduction of phenylethynyl extended π -conjugation length compared to FS11 and FS12. The emission spectra of FS11, FS12 and FS13 are also measured. The maximum emission wavelengths of FS11, FS12 and FS13 are 424 nm,

425 nm, 461 nm, respectively. The optical band gap (E_{0-0}) of the three compounds was calculated based on their spectroscopic data [37]. The E_{0-0} values of **FS11**, **FS12** and **FS13** are calculated to be 3.092 eV, 3.119 eV and 2.964 eV, respectively. Among the studied compounds, **FS13** shows the lowest energy gap, due to its extended π -conjugation structure. In contrast, **FS12** with the electron accepting –F on the diphenylamine branches show a higher HOMO-LUMO gap than **FS11** and **FS13**.



Fig. 2. Normalized absorption and fluorescence emission spectra of FS11, FS12 and

FS13 in dichloromethane with the concentration of 10^{-5} mol L⁻¹.

Compound	λ_{max}^{a} /nm	$\epsilon^{a}/10^{4}$ M ⁻¹ cm ⁻¹	E _{ox} ^b /V	E _{red} ^b /V	E _{ox,1/2} ^c /V	E ₀₋₀ ^d /eV	HOMO/V vs NHE ^e	LUMO /V vs NHE ^f
FS11	375	7.995	1.103	0.614	0.859	3.092	0.969	-2.123
FS12	373	6.722	1.123	0.645	0.884	3.119	0.994	-2.125
FS13	383	10.878	1.158	0.698	0.928	2.964	1.038	-1.926

Table 1. The spectroscopic and electrochemical data of FS11, FS12 and FS13.

^a The absorption spectra were measured in dichloromethane.

^b E_{ox} and E_{red} were calibrated from cyclic voltammograms.

^c $E_{ox,1/2} = (E_{ox} + E_{red})/2$

^d E_{0-0} values were estimated from the intersections of normalized absorption and emission spectra in dichloromethane, λ_{int} : E_{0-0} = 1240/ λ_{int} .

^e HOMO (vs NHE) were measured in CH_3CN and calibrated with ferrocene (0.63 V vs NHE).

^f LUMO (vs NHE) were estimated from calculated from LUMO=HOMO- $E_{0-0.}$



Fig. 3. UV-vis absorption spectra of FS11, FS12 and FS13 in dichloromethane.

The molar extinction coefficients (ϵ) changes of **FS11**, **FS12** and **FS13** in dichloromethane with the concentration 10⁻⁵ mol L⁻¹ are shown in Fig. 3. The molar extinction coefficients of the three truxene-cored compounds follow the order of

FS13 > **FS11** > **FS12**, and **FS13** (108780 M⁻¹cm⁻¹) has a much higher ε value at 300-400 nm than that of **FS11** (79950 M⁻¹cm⁻¹) and **FS12** (67220 M⁻¹cm⁻¹). Besides, UV-vis absorption spectra of **FS11**, **FS12** and **FS13** with the concentration of 10⁻⁵mol L⁻¹ in different organic solvents are shown in Fig. S1 (Supporting Information). **FS11**, **FS12** and **FS13** are insensitive to the solvent polarity, indicating that the charge transfer do not happen in ground-states of the studied compounds [24, 38]. The fluorescence spectra of compounds FS11, FS12 and FS13 in different organic solvents have also been investigated, as shown in Fig.S2 (Supporting Information). Fig.S2 shows the fluorescence spectra of three compounds are sensitive to solvent polarity. The maximum emission wavelengths in different organic solvents shows a red shift in the order of Toluene<THF<Acetone<CH₂Cl₂. This result indicates that the charge transfer of the studied compounds may occur in excited state.

3.2. Quantum chemical calculation, electrochemical and thermal properties

To gain insight into the electronic properties and geometries of FS11, FS12 and FS13, quantum chemical calculations on based on DFT at the B3LYP/6-31G level were carried out. Their geometric structures were optimized. All structural optimization and energy calculations were performed using the GAUSSIAN 09 program. The optimized structures and the frontier orbitals of FS11, FS12 and FS13 are shown in Fig. 4. The highest occupied molecular orbital (HOMO) of FS11, FS12 and FS13 and FS13 almost delocalize over the whole molecule, while the lowest unoccupied molecular orbital (LUMO) is mainly transferred to the truxene core and the longer functional phenylamine chain. The representative dihedral angles and bond lengths of

FS11, **FS12** and **FS13** are presented in Fig. S3 (Supporting Information) and Table S1. The dihedral angle between the truxene core and the diphenylamine is reduced in the order of **FS11** (141.361°) > **FS12** (140.629°) > **FS13** (139.381°). **FS13** has the smallest dihedral angle between the truxene core and the diphenylamine, and it exhibits a rigid three-dimensional structure with phenylethynyl. The dihedral angle between the phenyl ring of phenylamine and phenylethynyl in **FS13** is 174.066°. The dihedral angle between the phenyl ring of phenylamine and tolyl in **FS11** is -147.094°, and that between the phenyl ring of phenylamine and fluorophenyl in **FS12** is -145.755°. The bond lengths between the truxene core and the diphenylamine is increased in the order of **FS11** (1.426 Å) < **FS12** (1.427 Å) < **FS13** (1.429 Å). The result indicates that **FS13** exhibits a longer conjunction length than **FS11** and **FS12**.

To further evaluate the potential applicability in electronic devices, the electrochemical properties of the three truxene-based compounds were studied by cyclic voltammetry, and their CV diagrams are shown in Fig. 5. The corresponding electrochemical data are listed Table 1. All the compounds display a reversible oxidation-reduction behavior. The HOMO levels of **FS11**, **FS12** and **FS13** corresponding to the oxidation potentials (E_{ox}) was 0.969 eV, 0.994 eV and 1.038 eV, and the LUMO level of **FS11**, **FS12** and **FS13** was -2.123 eV, -2.125 eV and -1.926 eV, respectively. This result suggests the different substituted groups on the diphenylamine have an effect on their redox ability, and the oxidation potentials follow the order of **FS13** > **FS12** > **FS11**. It can be concluded that substantial electronic communication exists between the diphenylamine donor and the truxene



core in the studied molecules.

Fig. 4. The frontier molecular orbital distributions of FS11, FS12 and FS13 optimized

by DFT calculations at the B3LYP/6-31G level.



Fig. 5. Cyclic voltagrams of **FS11**, **FS12** and **FS13** in dichloromethane with ferrocene as a reference at a scan speed of 25 mV/s.

The thermal stability of **FS11**, **FS12** and **FS13** has been analyzed by differential scanning calorimetry (DSC) and thermogravimetry (TG). The corresponding results of DSC and TG were plotted in Fig. 6, respectively. In Fig. 6 (a), the glass transition temperature (T_g) of compounds **FS11-13** are 153 °C, 153 °C and 154 °C, respectively. The T_g values of the three compounds are high, suggesting that a good morphological stability owing to the inflexible structure of the truxene core. In Fig. 6 (b), TG curves shows compounds **FS11-13** have a high decomposition temperature (T_d) at 422 °C, 440 °C and 423 °C, respectively. It is also found that the introduction of fluorine group obviously enhance the thermostability properties of **FS12** [39].



Fig. 6. (a) DSC and (b) TG curves of compounds FS11-13.

3.3. Two-photon induced fluorescence properties

The 2PA properties of **FS11**, **FS12** and **FS13** have been studied by using two-photon induced fluorescence (2PEF) spectra. The three compounds exhibit obvious 2PEF, and their σ 2 values with the excited wavelengths ranging from 720 nm to 820 nm per 10 nm were depicted in Fig.7 and Table S2. The maximum σ 2 values

($\sigma 2_{max}$) for FS11, FS12 and FS13 are exhibited at the excited wavelength of 750 nm, which are 260 GM, 204GM and 367 GM, respectively. FS13 also yields a $\sigma 2_{max}$ of 36 GM and 15 GM at 840 nm and 860 nm, respectively. The result is consistent with the linear absorptions of these compounds. According to the references [23-26], the truxene-cored compounds can give a very good 2PA response from 27GM to 5100 GM. In our studied compounds, the asymmetric diphenylamines substituted on the truxene central core enhance the overall molecular rigidity, and the "pull-push" effect of the electron-withdrawing and electron-donating substituents can increase charge transfer between the asymmetric diphenylamine branch and the truxene core. FS11, FS12 and FS13 yield a good 2PA property.



Fig. 7. Two-photon absorption cross sections of FS11, FS12 and FS13 in acetonitrile.

4. Conclusions

In this paper, three-branched compounds based on a truxene core and asymmetric diphenylamines were prepared (FS11, FS12 and FS13). The asymmetric

diphenylamine includes one phenyl of diphenylamine substituted by methoxy group and the other phenyl substituted by tolyl, fluorophenyl and phenylethynyl for FS11, FS12 and FS13, respectively. The introduction of electron donor (-OMe), electron acceptor (-F) and π -bridge (-C=C-) has an positive effect on their charge transfer properties. The one-photon absorption maxima of FS11, FS12 and FS13 (charge transfer band) are 375 nm, 373 nm and 383 nm, respectively. The corresponding molar extinction coefficients of the three truxene-cored compounds follow the order of FS13 (108780 $M^{-1}cm^{-1}$) > FS11 (79950 $M^{-1}cm^{-1}$) > FS12 (67220 $M^{-1}cm^{-1}$). FS13 has an extended a longer π -conjugation length than FS11 and FS12, which is in consistent with the lowest energy gap among three compounds according to CV curves. The geometric structures optimized by DFT theoretical calculation indicate that these star-shaped truxene derivatives exhibit a rigid spatial structure. DSC and TG results show that they exhibit high T_g (> 150 °C) and T_d (> 420 °C) temperatures. The 2PA cross section maxima are observed at the excited wavelength of 750 nm from the 2PEF measurement results, which are 260 GM, 204GM and 367 GM for FS11, FS12 and FS13, respectively. Therefore, the studied truxene-diphenylamine compounds have a great potential in the optoelectronics fields.

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Graphical abstract

Highlights

- * Three truxene-cored compounds with asymmetric diphenylamines were prepared.
- * The "pull-push" structure promotes charge transfer.
- * All three compounds exhibit strong two-photon excited fluorescence.